Thermal Analysis
phase diagrams

R W McCallum

Ames Laboratory

And

Materials Science and Engineering

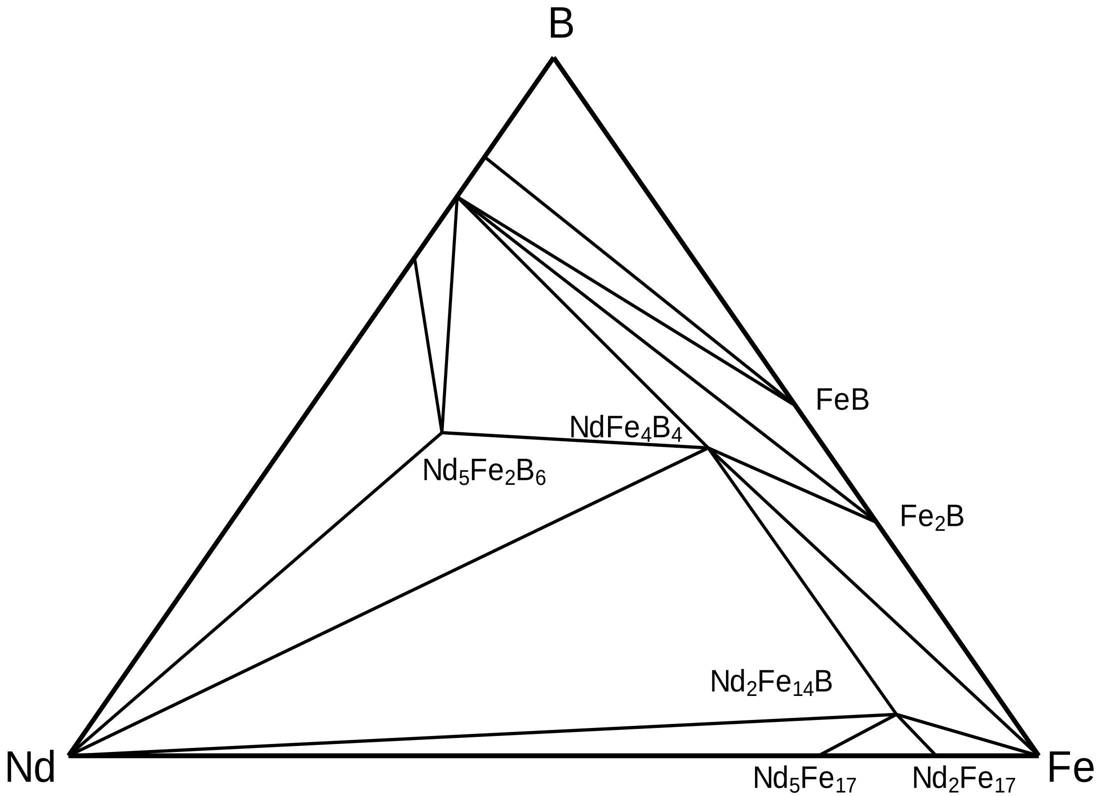
Why Phase Diagrams

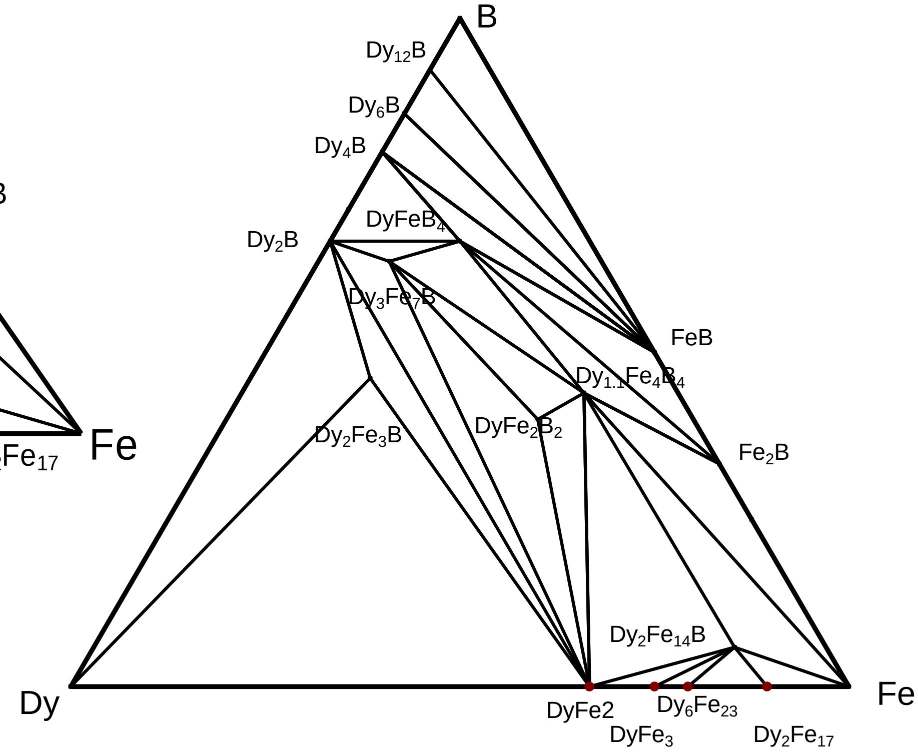
- Thermal analysis gives us information about phase transitions which are the lines on a phase diagram
- I never saw one in a physics class

Why should I care?

- If you wish to measure the intrinsic properties of an intermetallic compound you need
  - Single phase
  - Homogenous
- Often you can't just melt the elements together
  - Why do you need to anneal some samples?
  - At what temperature do you heat treat?
  - How long will it take?

Typical ternary phase diagram at constant temperature





What is a phase

- In the physical sciences, a **phase** is a set of states of a macroscopic physical system that have relatively uniform chemical composition and physical properties (i.e. density, crystal structure, index of refraction, and so forth).

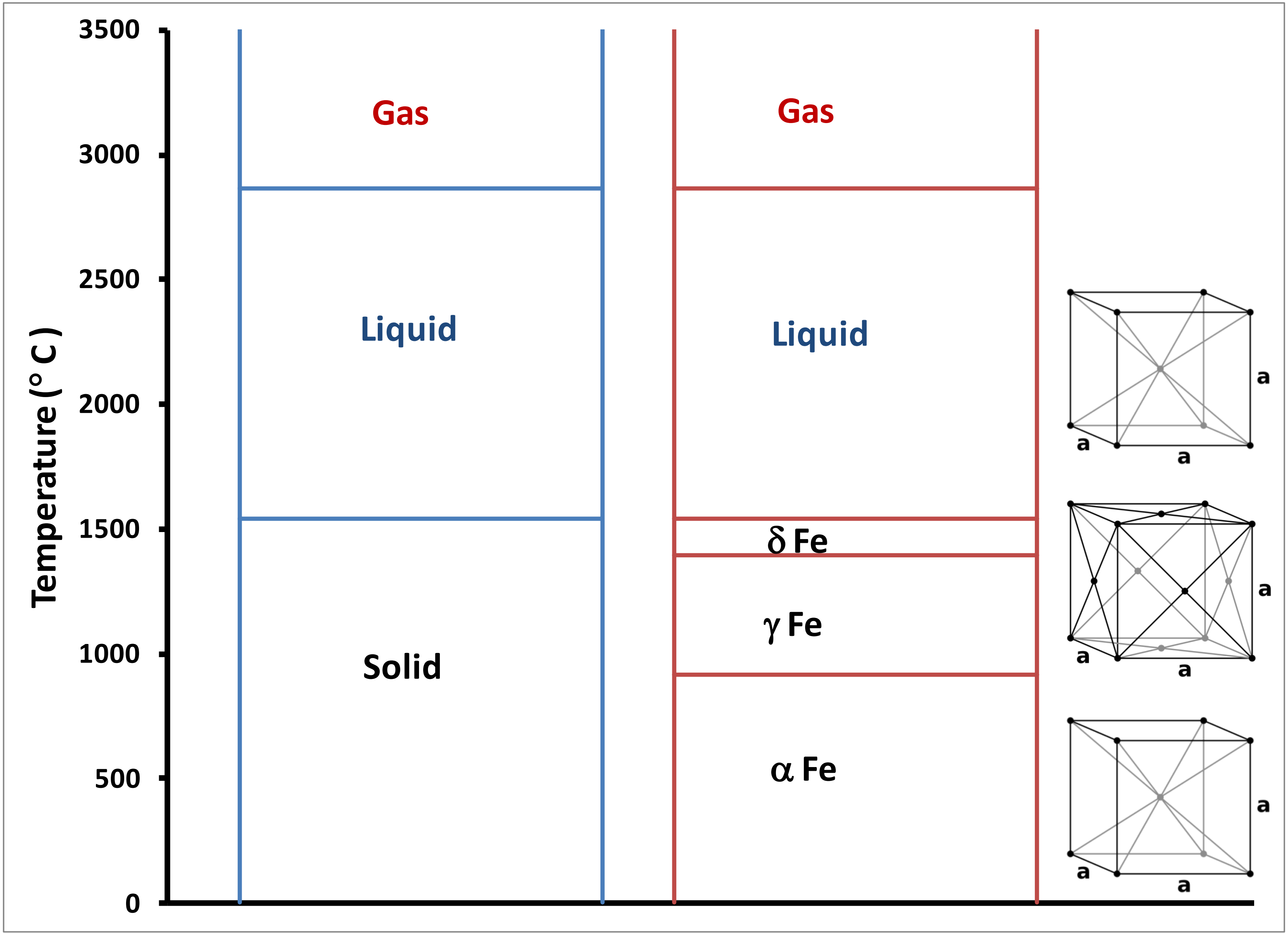
From Wikipedia,

What is a phase

- Phases are sometimes confused with states of matter, but there are significant differences. States of matter refers to the differences between gases, liquids, solids, plasma, etc. If there are two regions in a chemical system that are in different states of matter, then they must be different phases. However, the reverse is not true — a system can have multiple phases which are in equilibrium with each other and also in the same state of matter.

From Wikipedia,

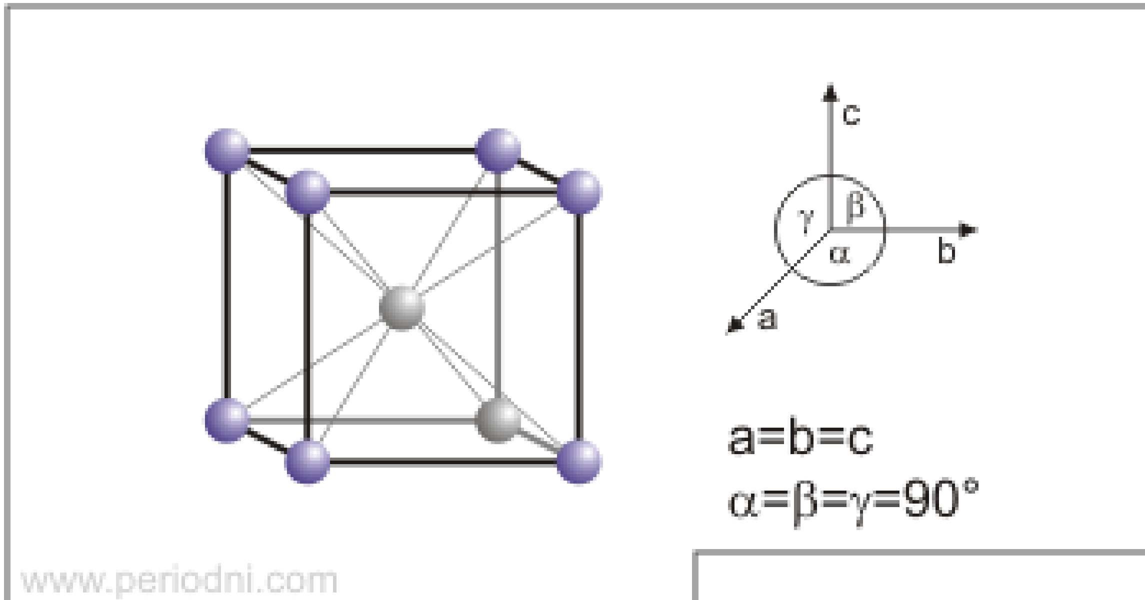
State vs Phase

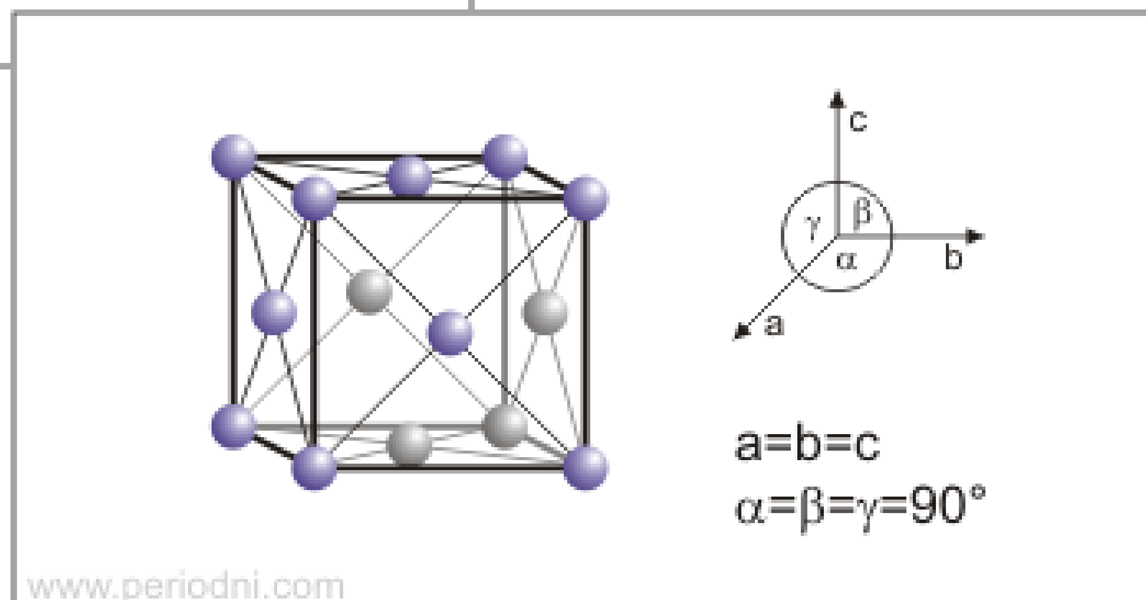


What distinguishes a phase

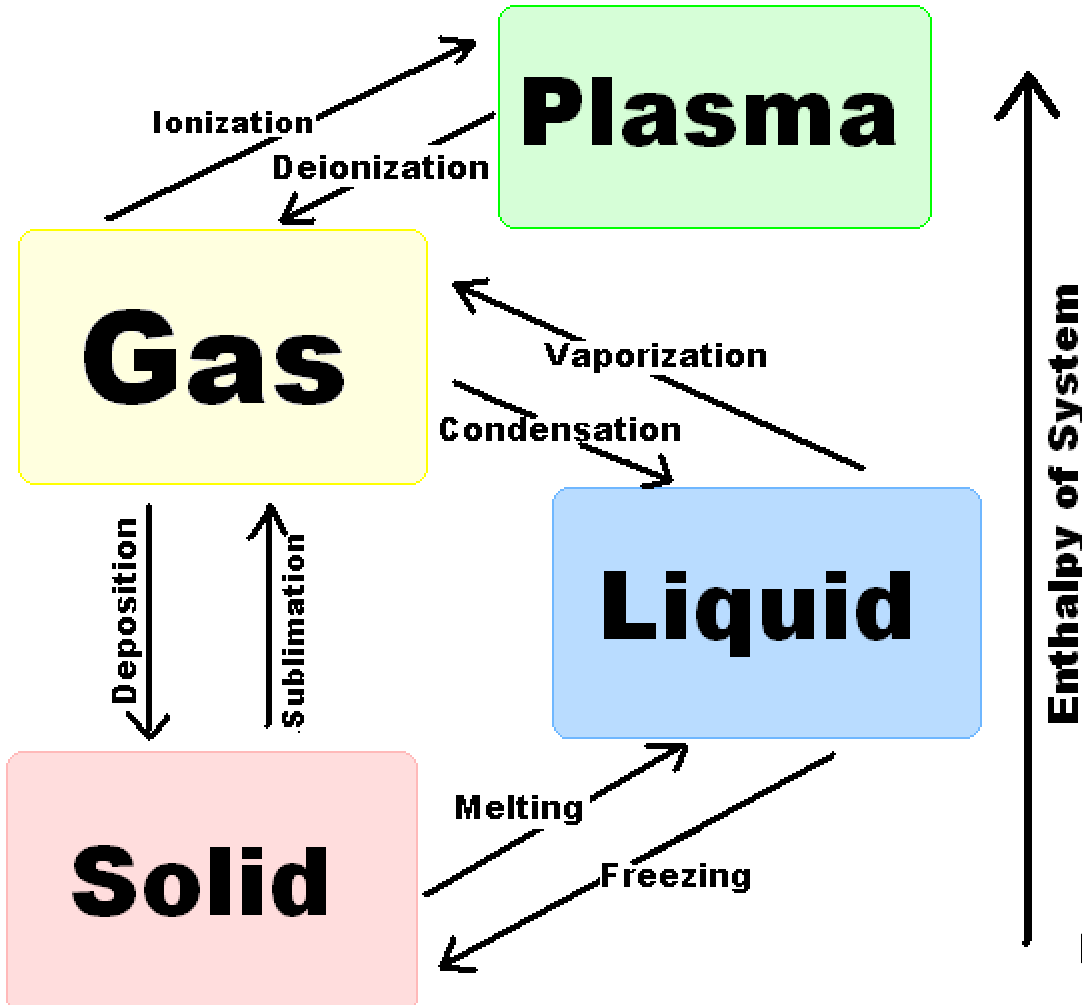
- two different states of a system are in different phases
  - transforming between states results in an abrupt change in physical properties.
- two states are in the same phase
  - transforming between states results in gradual change in physical properties.
- exceptions to this definition
  - for example the liquid-gas critical point.

Crystal Structure





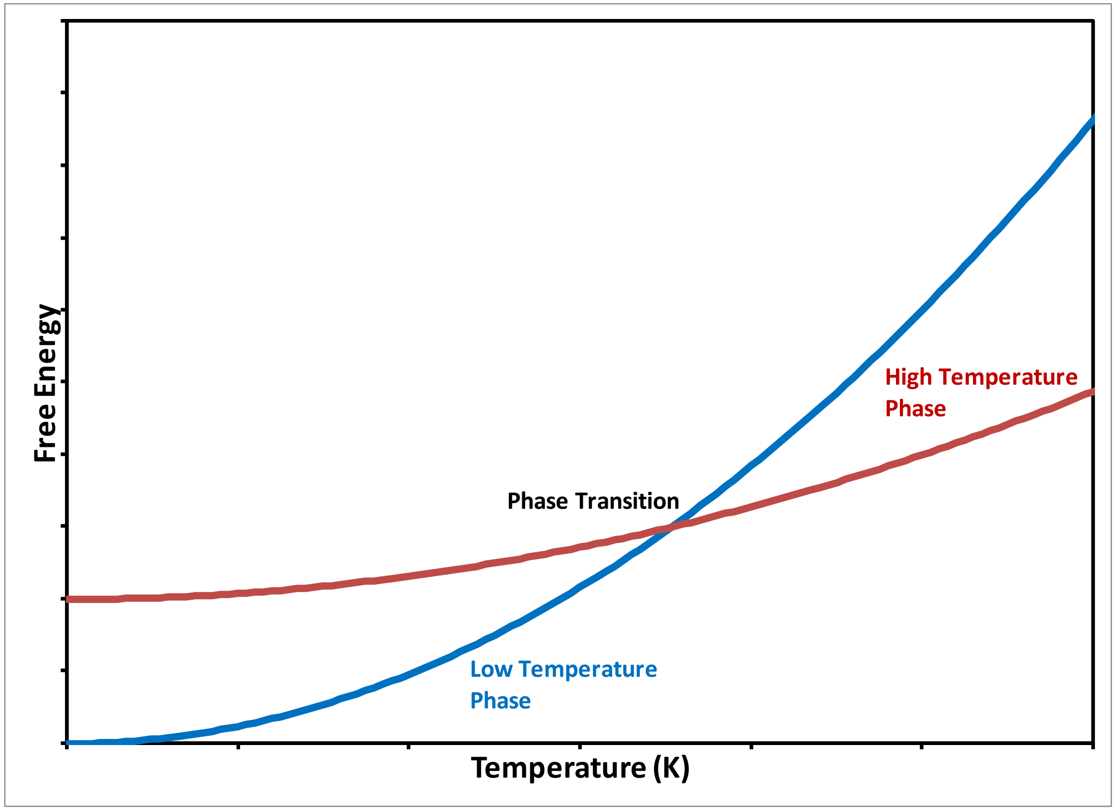
Phase transition



From Wikipedia,

Phase Transition

- At phase-transition point
  - the two phases have identical free energies
  - equally likely to exist.
- Below the phase-transition point
  - Low temperature phase is more stable state of the two.
- Above the phase-transition point
  - High temperature phase is more stable state of the two.



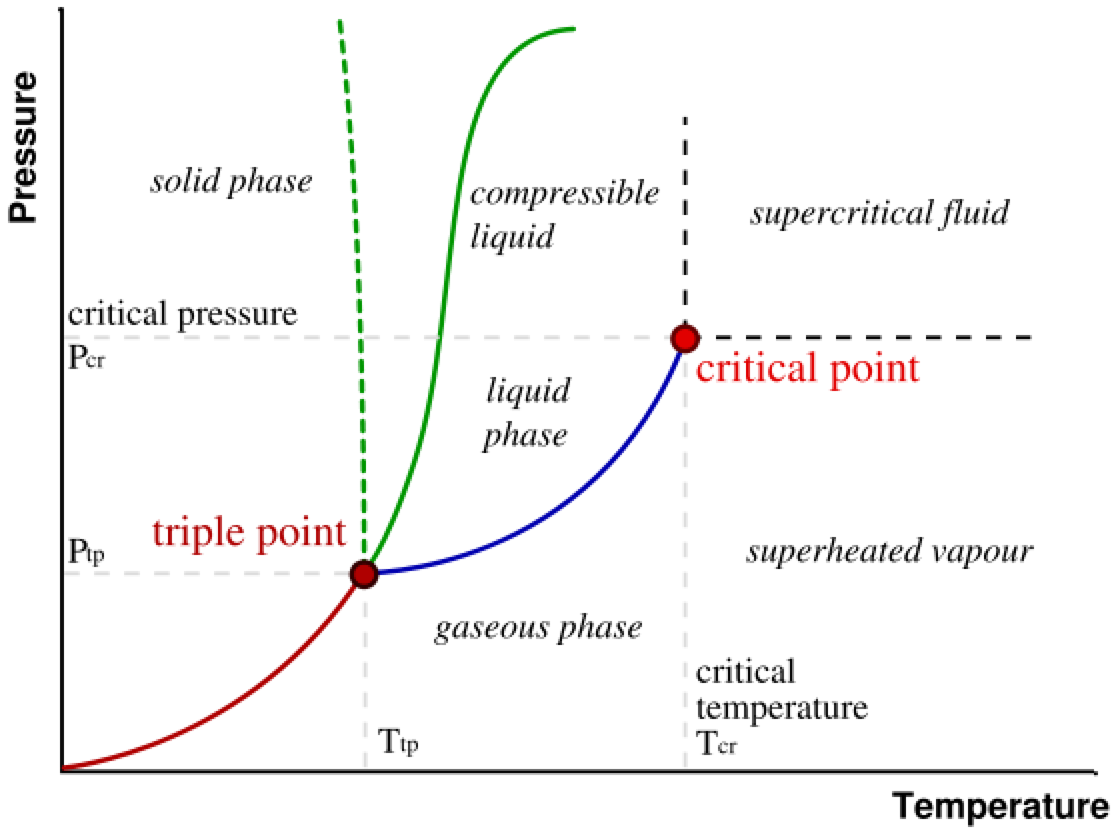
Ehrenfest's classification of phase transitions

- phase transitions labeled by the lowest derivative of the free energy that is discontinuous at the transition.
- First-order phase transitions
  - exhibit a discontinuity in the first derivative of the free energy with a thermodynamic variable.
  - solid/liquid/gas transitions are first-order transitions
    - because they involve a discontinuous change in density (which is the first derivative of the free energy with respect to chemcial potential.)
- Second-order phase transitions
  - continuous in the first derivative
  - exhibit discontinuity in a second derivative of the free energy.
    - example, the ferromagnetic phase transition in materials such as Fe,
      - **magnetization** *(the first derivative of the free energy with the applied magnetic field strength)*, increases continuously from zero as the temperature is lowered below Tc
      - **magnetic susceptibility** *(the second derivative of the free energy with the field)* changes discontinuously.

Types of phase transitions

- first-order phase transitions
  - involve a latent heat
    - system either absorbs or releases a fixed (and typically large) amount of energy.
    - the temperature of the system will stay constant as heat is added or released.
  - "mixed-phase regimes“
    - in which some parts of the system have completed the transition and others have not.
      - a pot of boiling water:
        - » turbulent mixture of water and water vapor bubbles.

Single component



Gibbs' Phase Rule

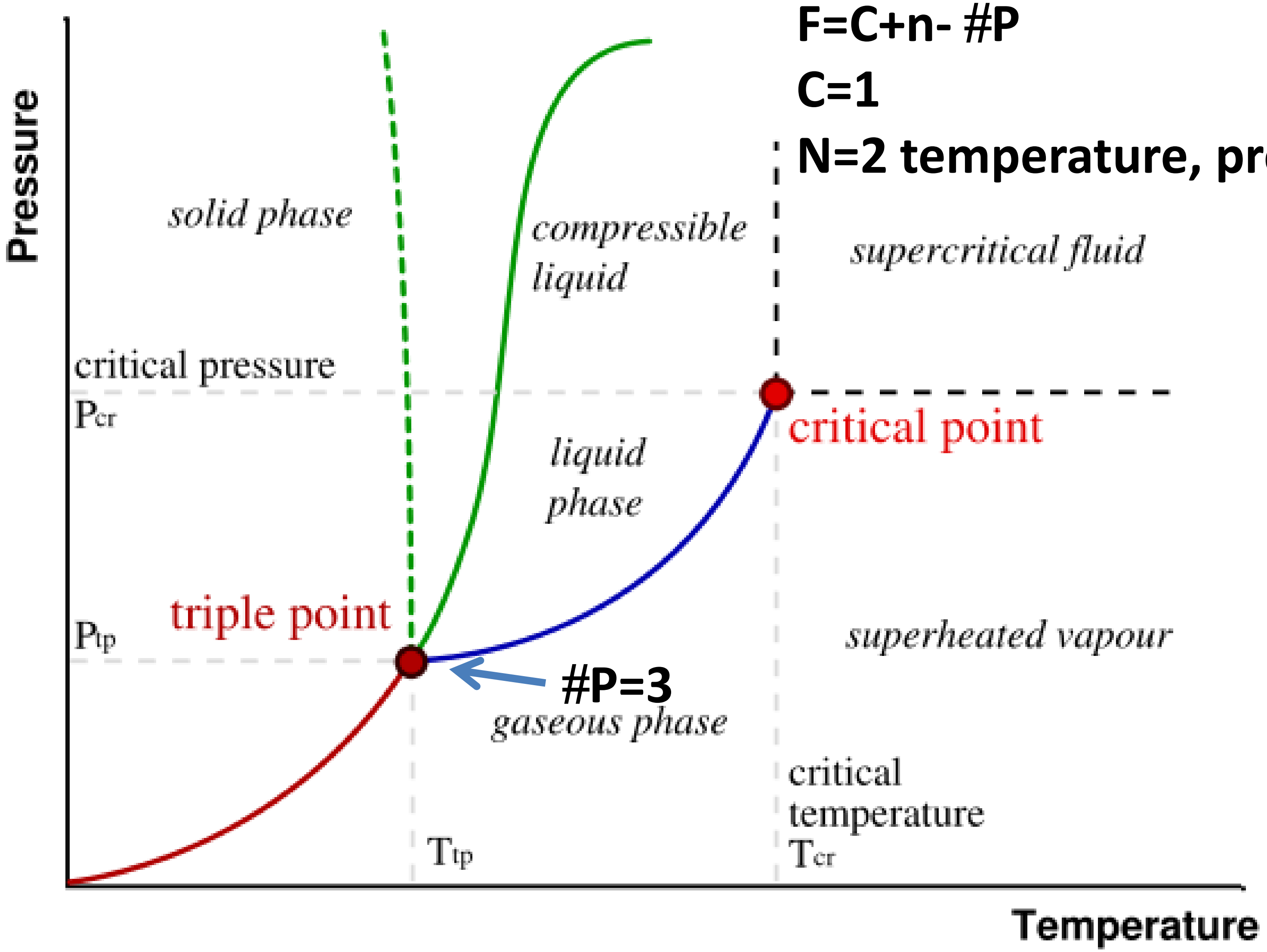
- F=C+n-#P
  - F ⇔ Degrees of freedom
    - Temperature
    - Pressure
    - composition
  - C ⇔ number of components
  - n ⇔ for the main control parameters
    - Temperature
    - Pressure
      - For high melting materials vapor pressure is negligible n=1
      - for high vapor pressure materials n=2
  - # P ⇔ number of phases
- Binary phase diagram
  - C=2

Single component

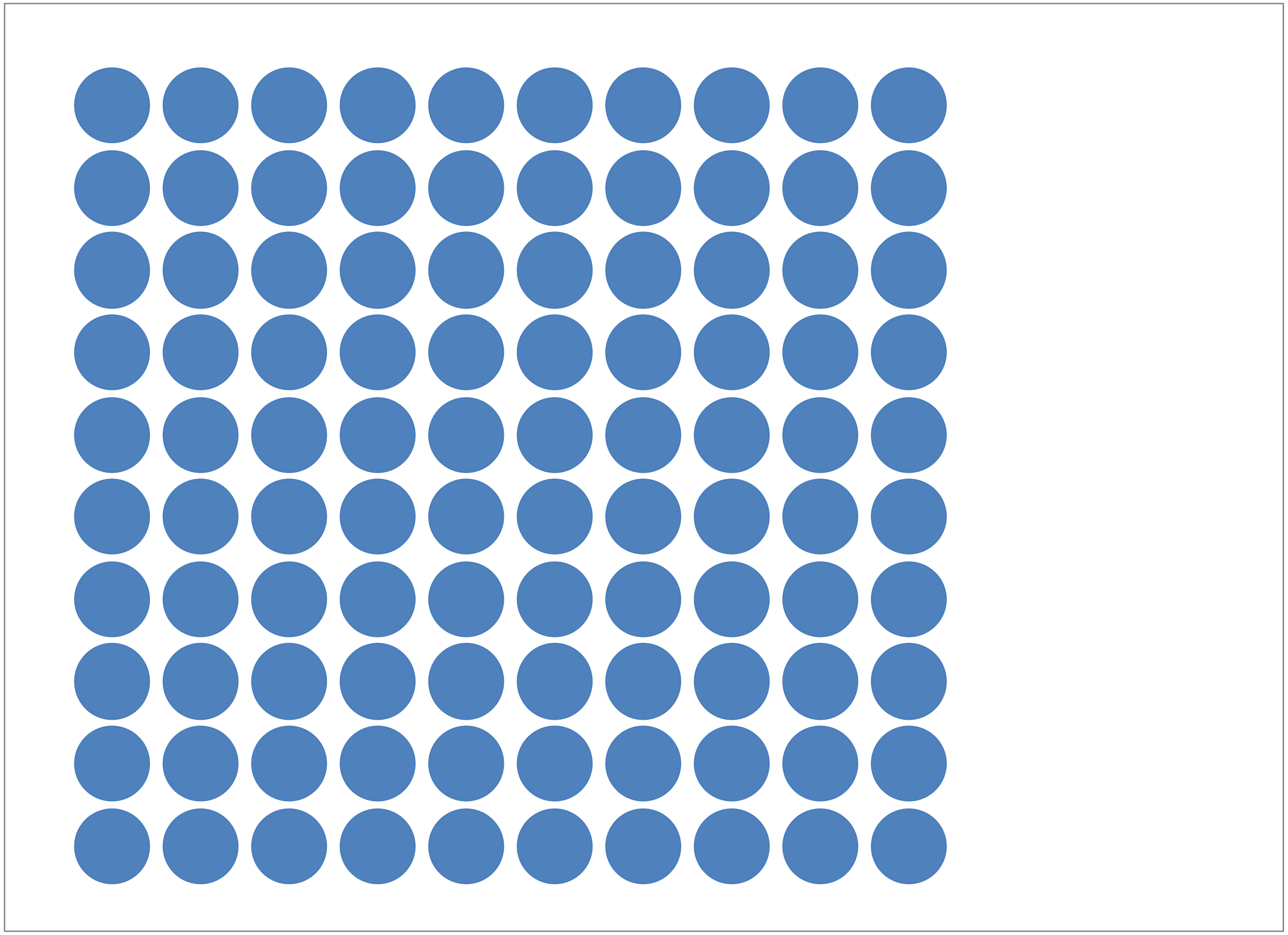
F=C+n- #P

C=1

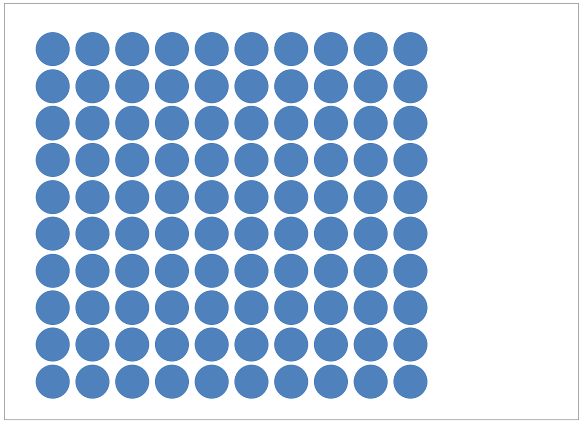
N=2 temperature, pressure

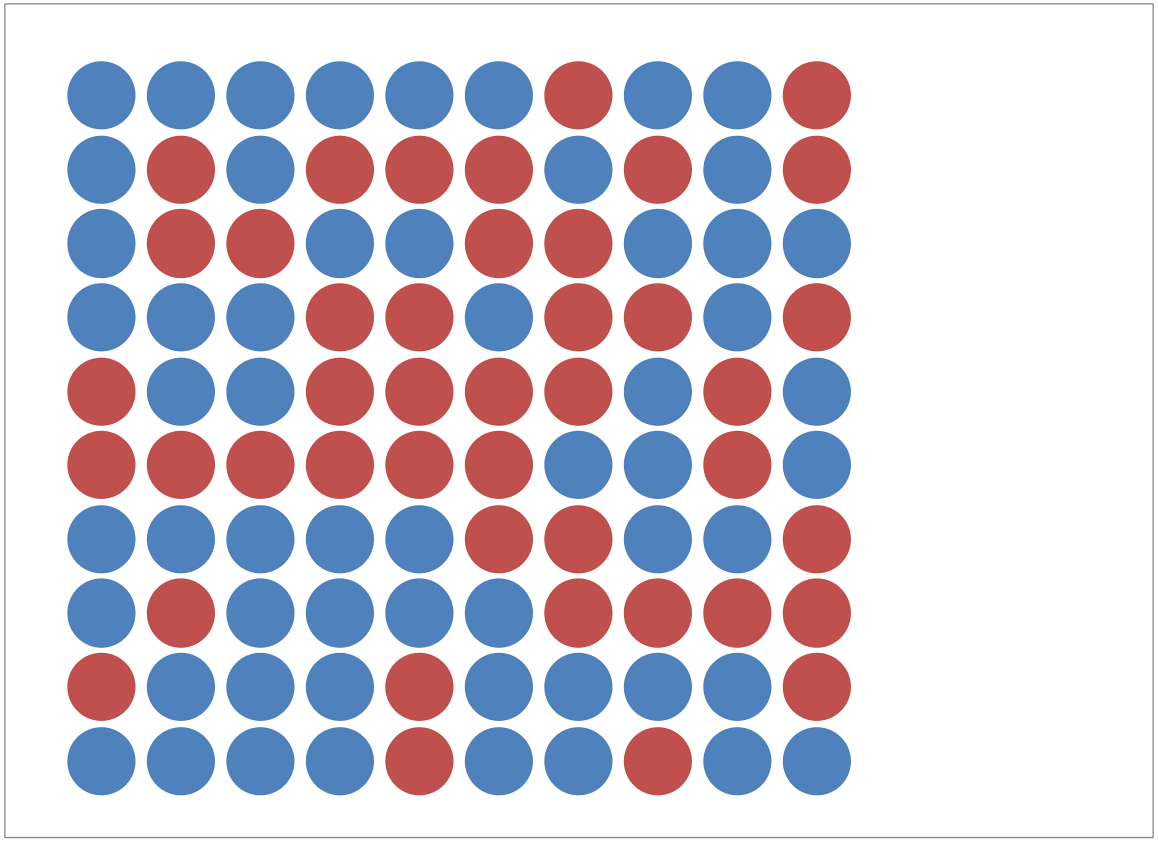


1 component

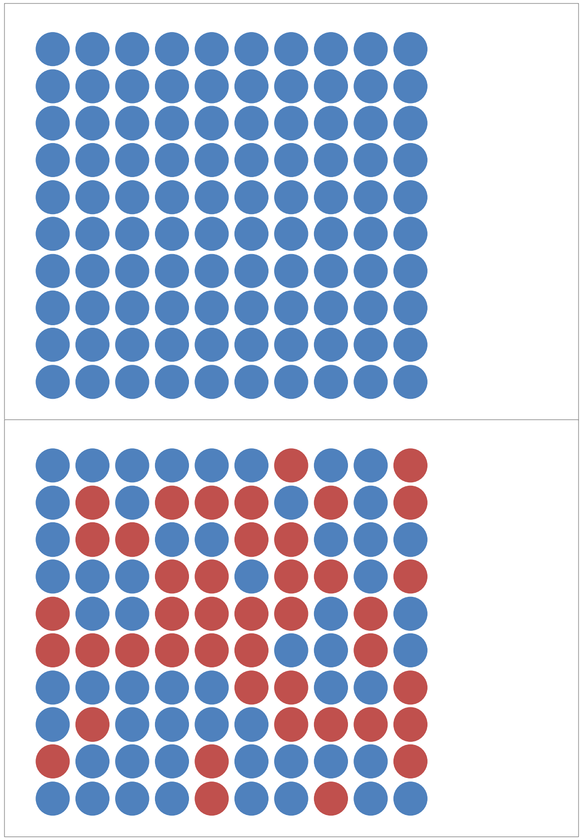


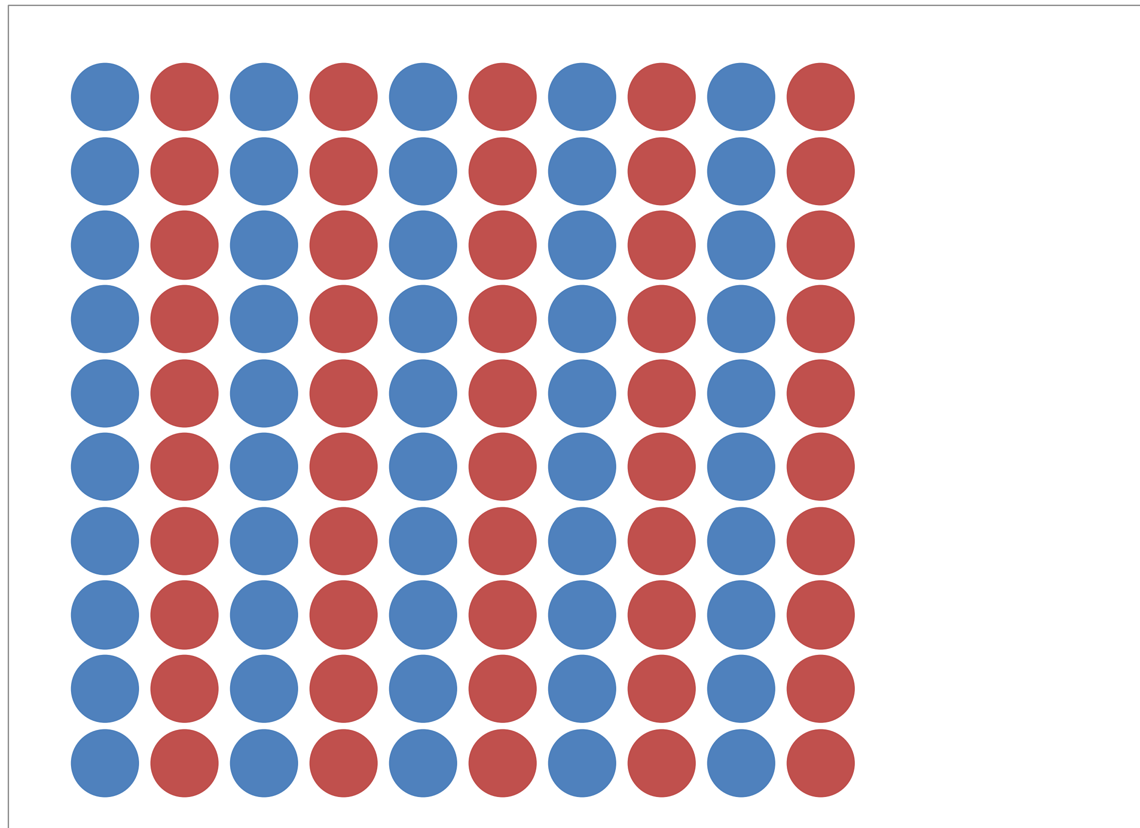
2 component solid solution (random)



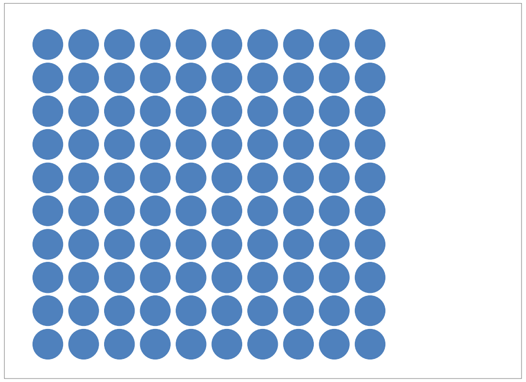


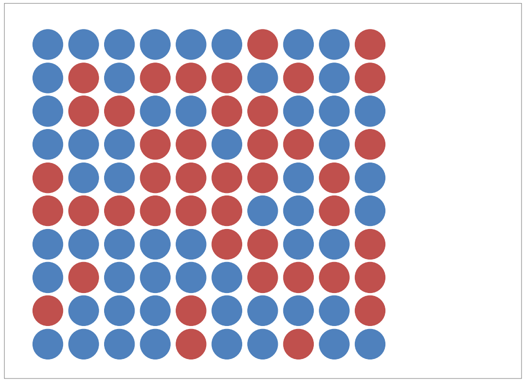
2 component ordered

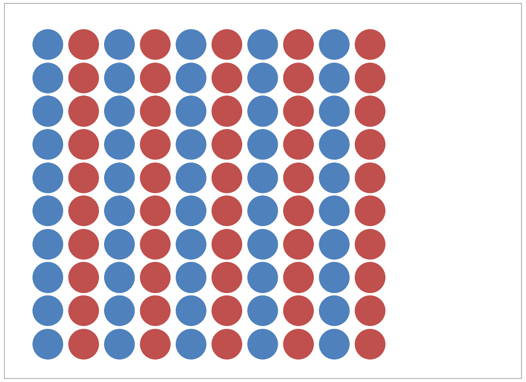


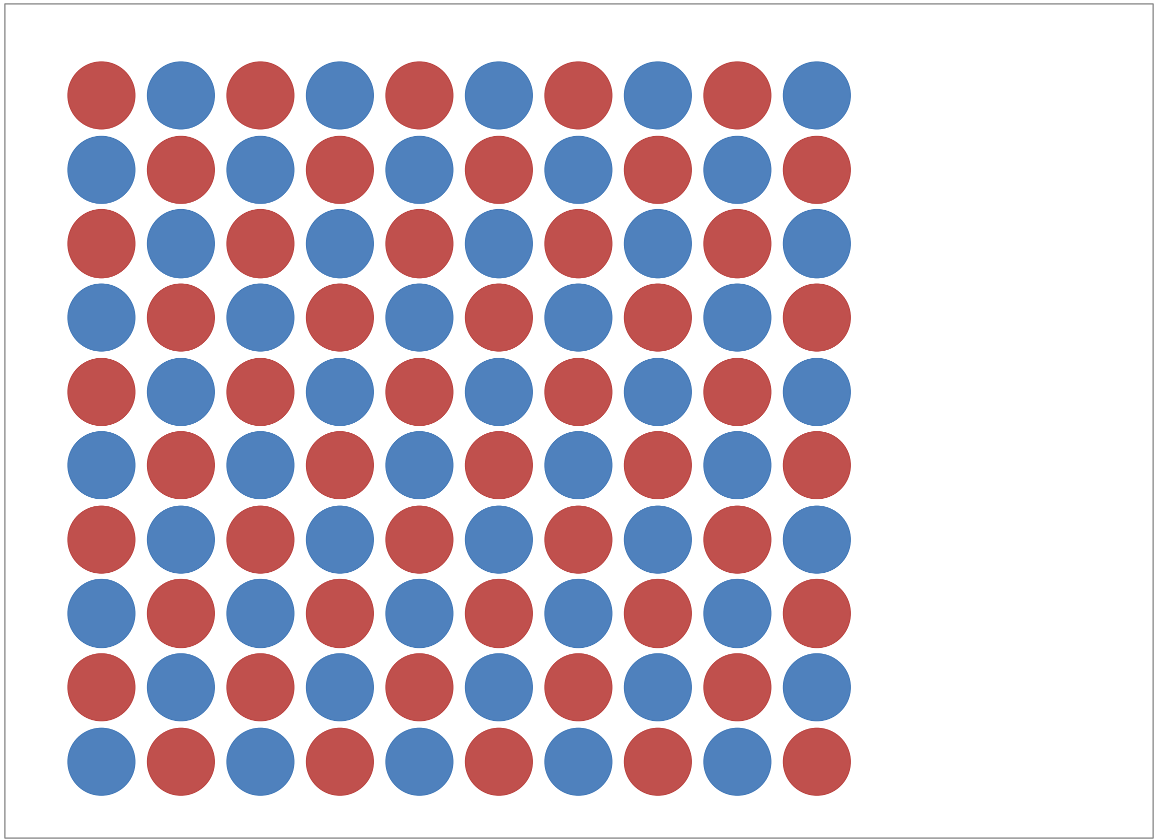


2 component ordered

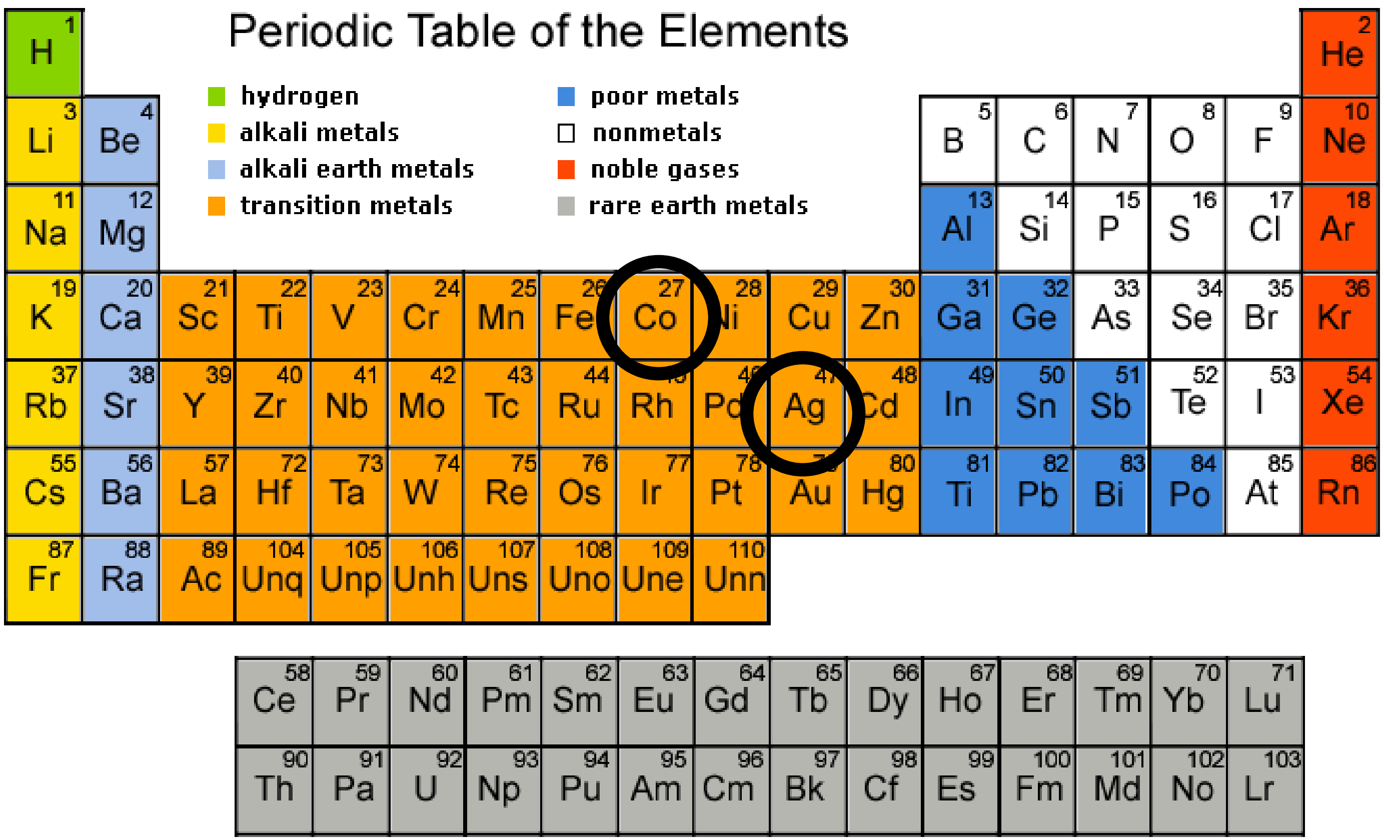




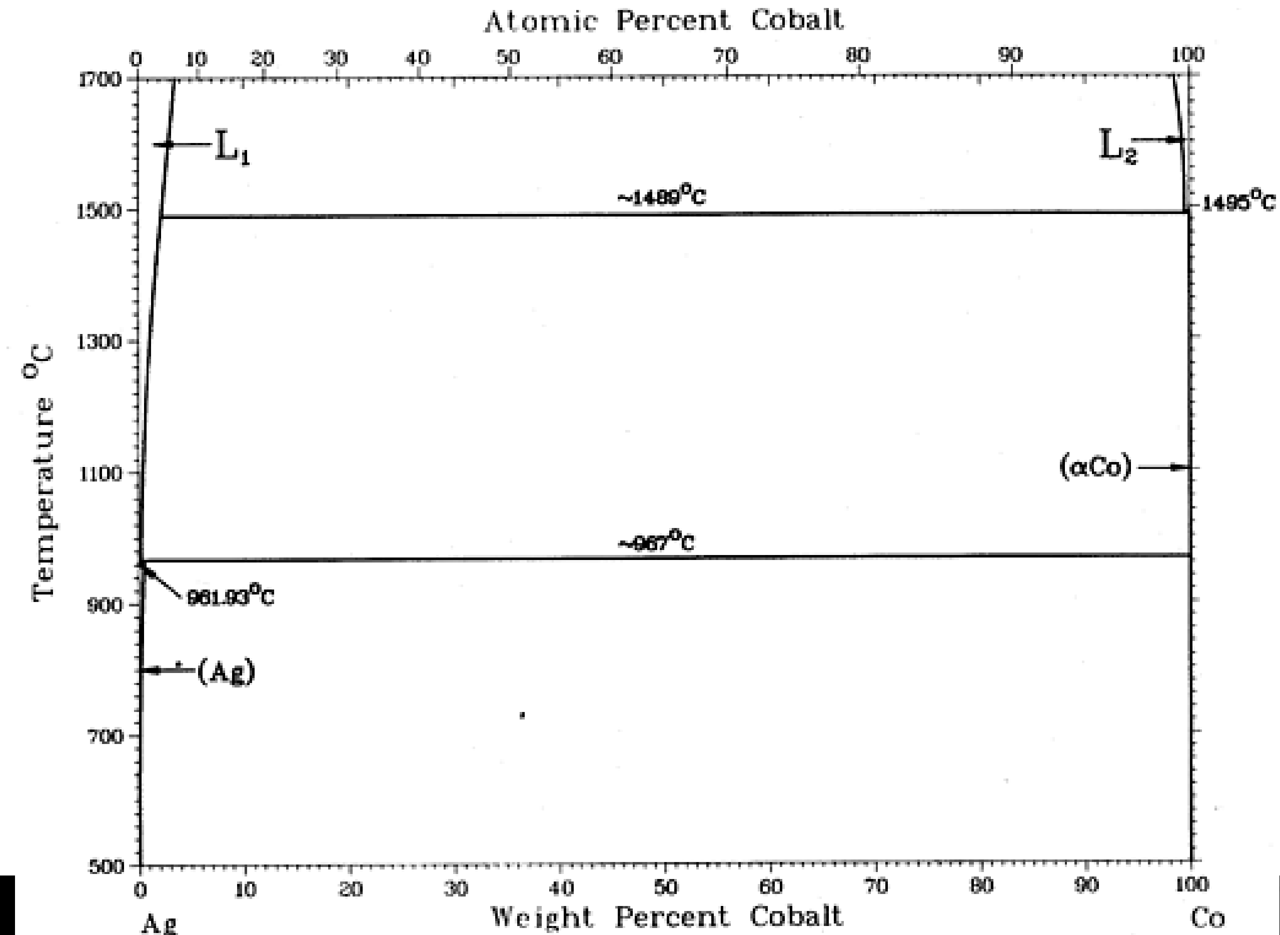




Two components

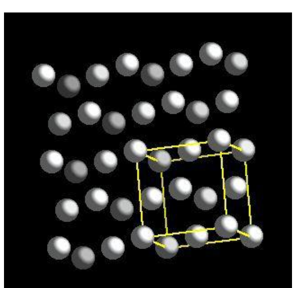


Immiscible no compounds



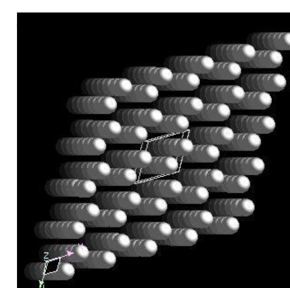
FCC

Ag^{+2} 0.89 Å

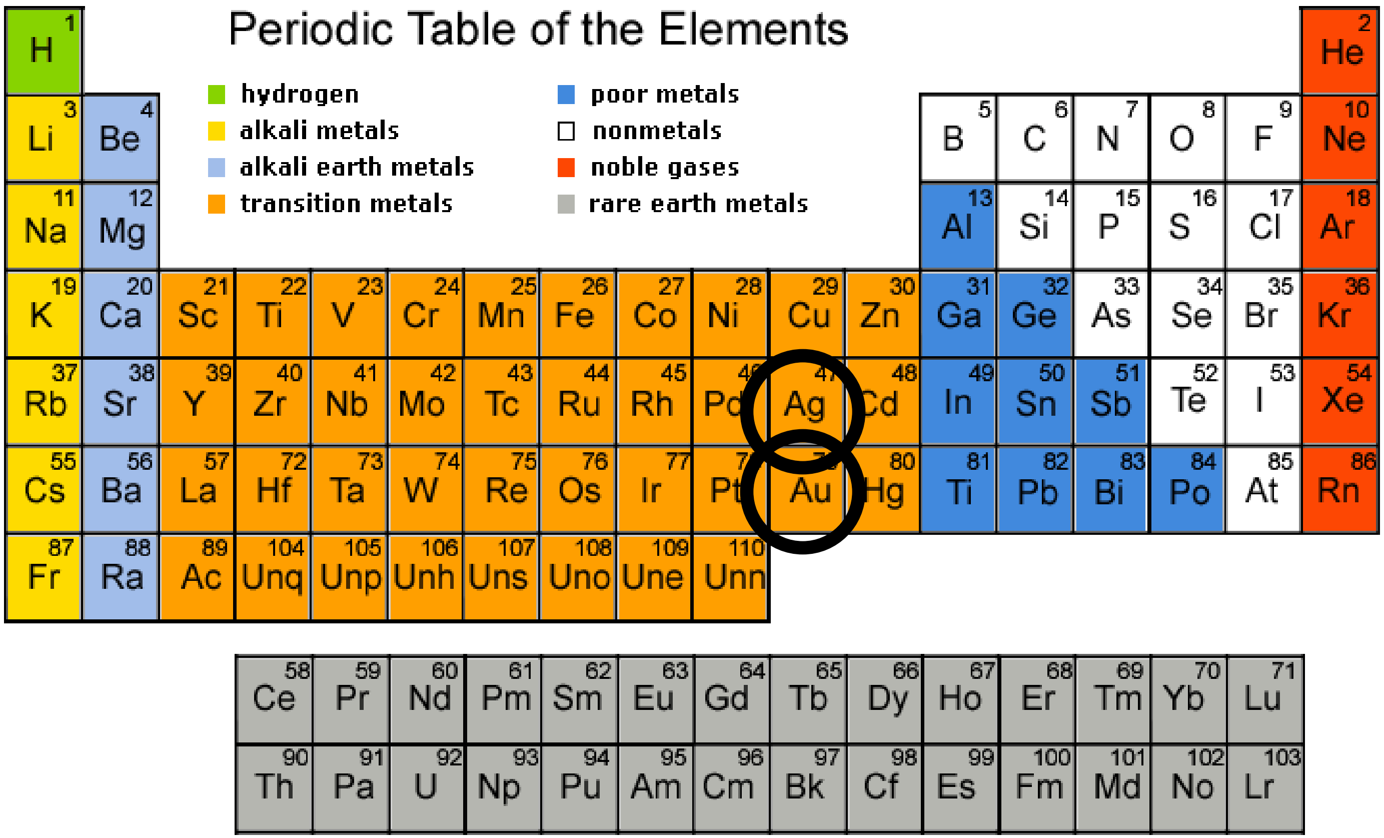


Hexagonal

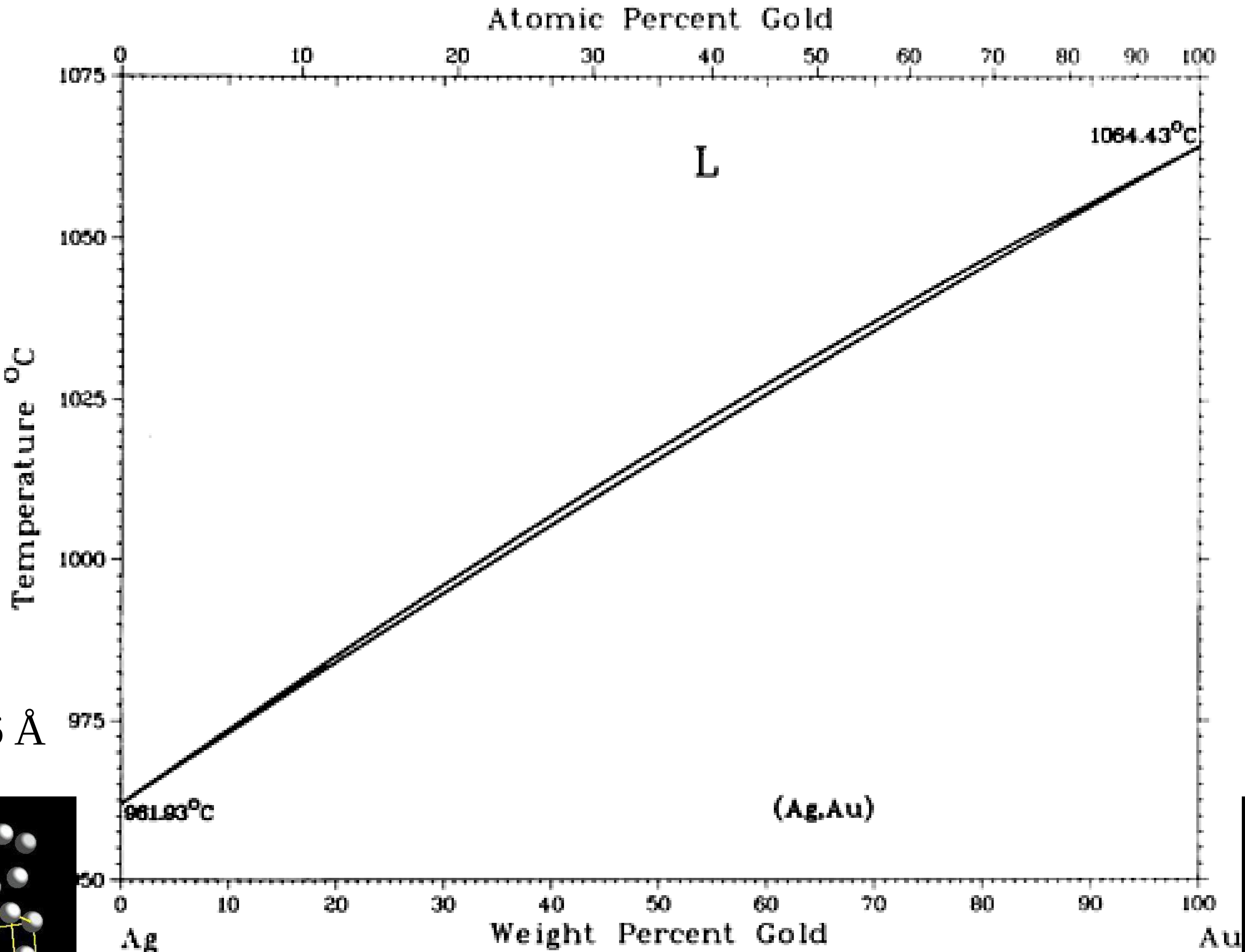
Co^{+2} 0.72 Å



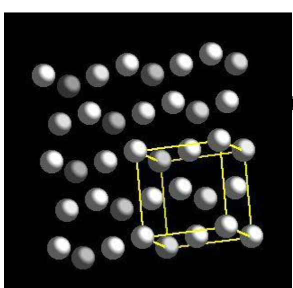
Two components



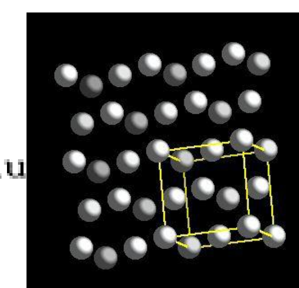
Solid Solutions



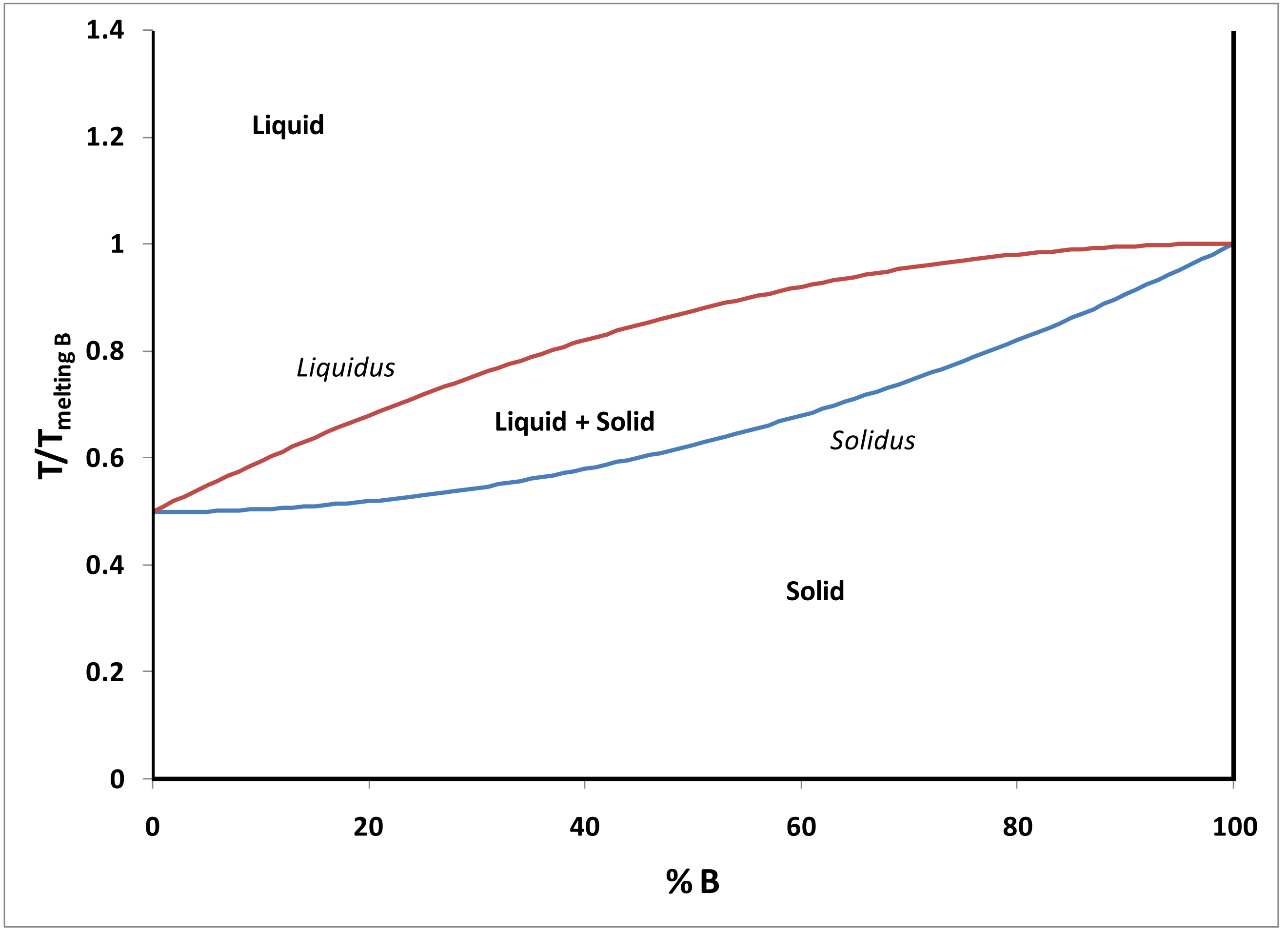
Ag^{+1} 1.26 Å



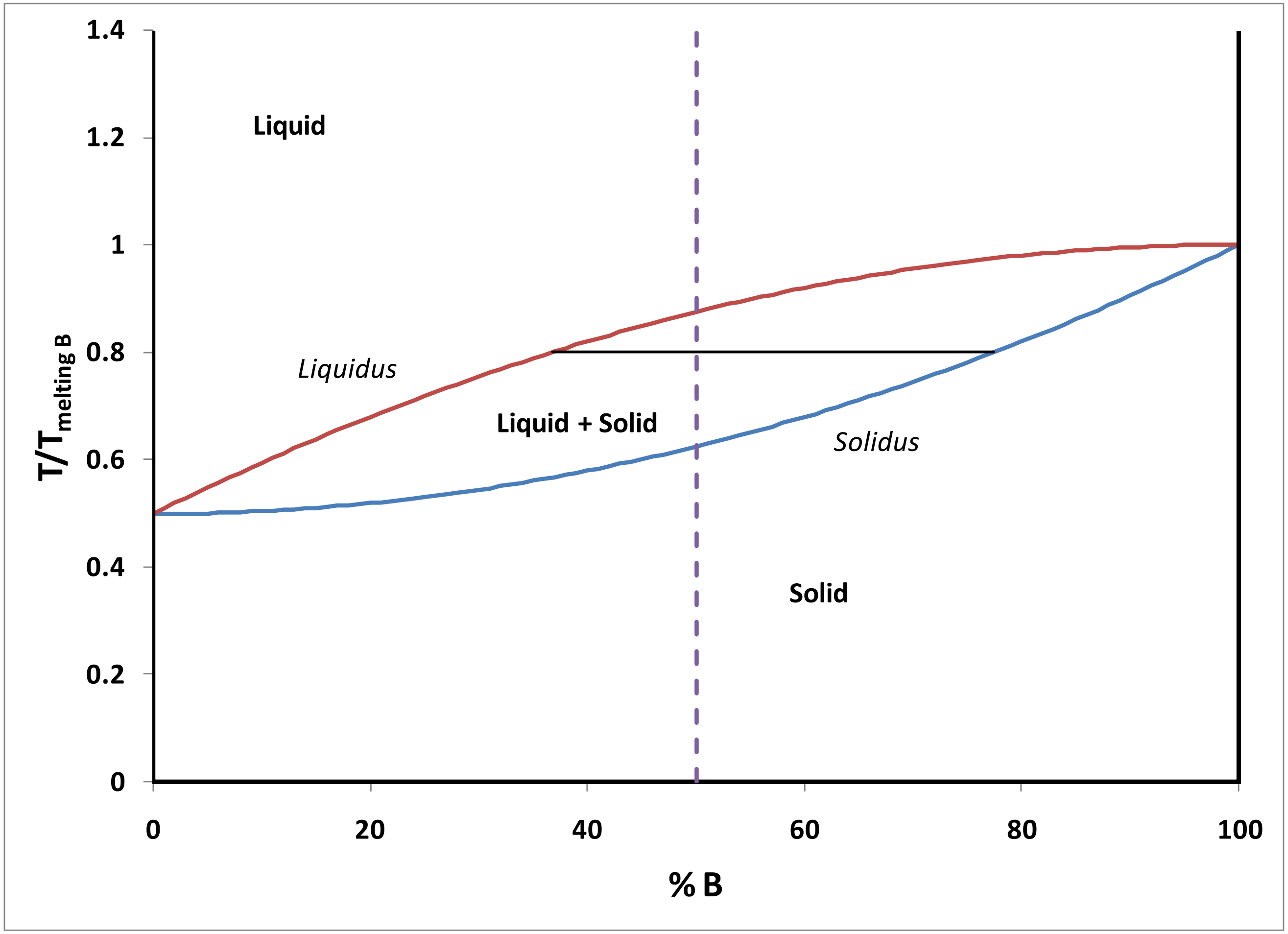
Au^{+1} 1.37 Å



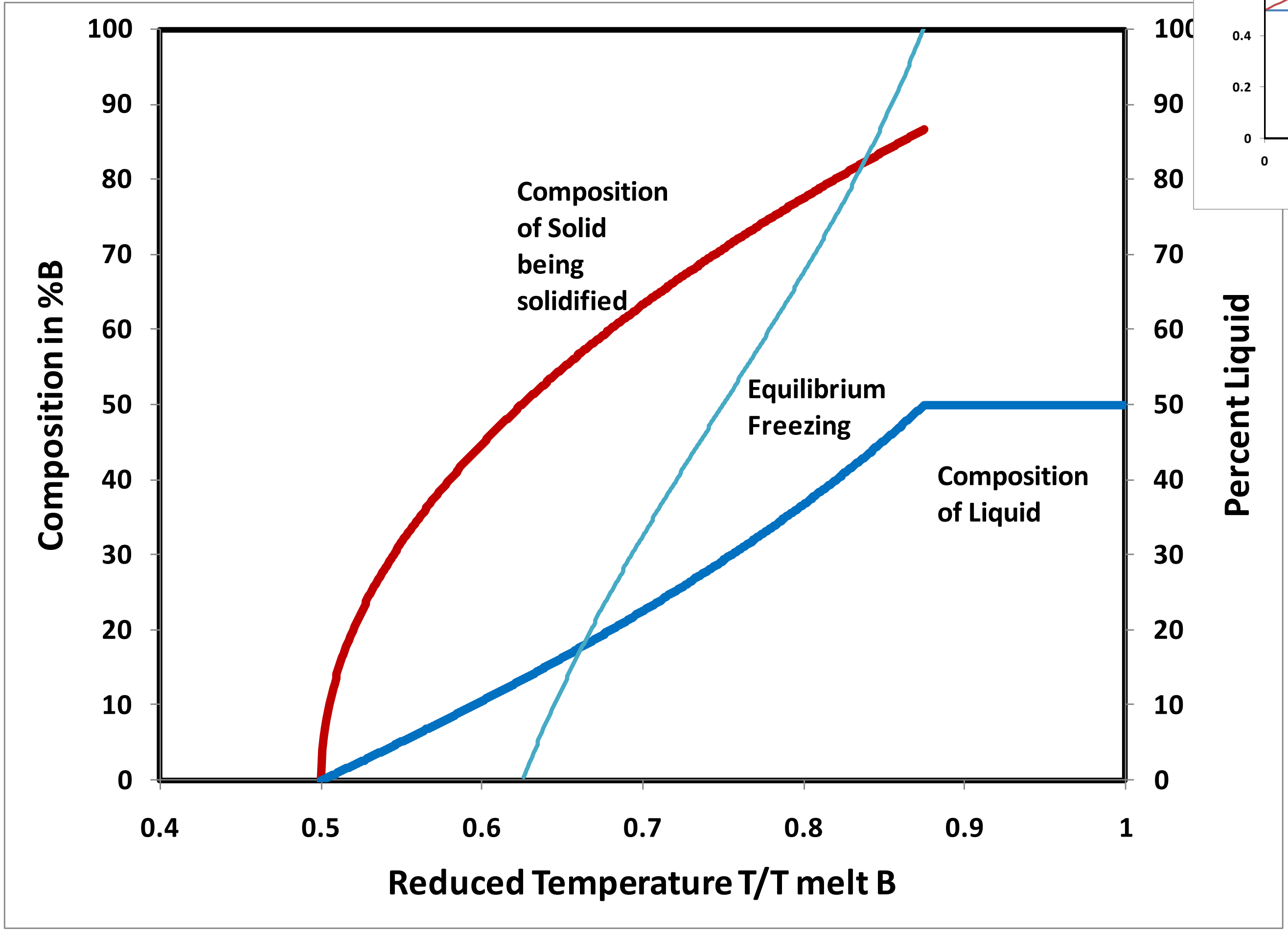
Solid Solution

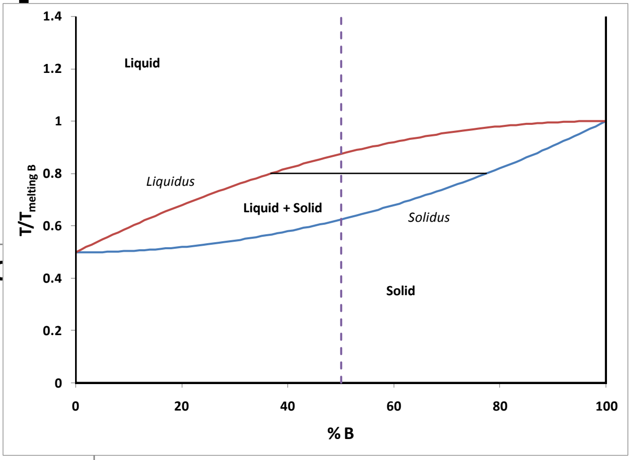


Solid Solution

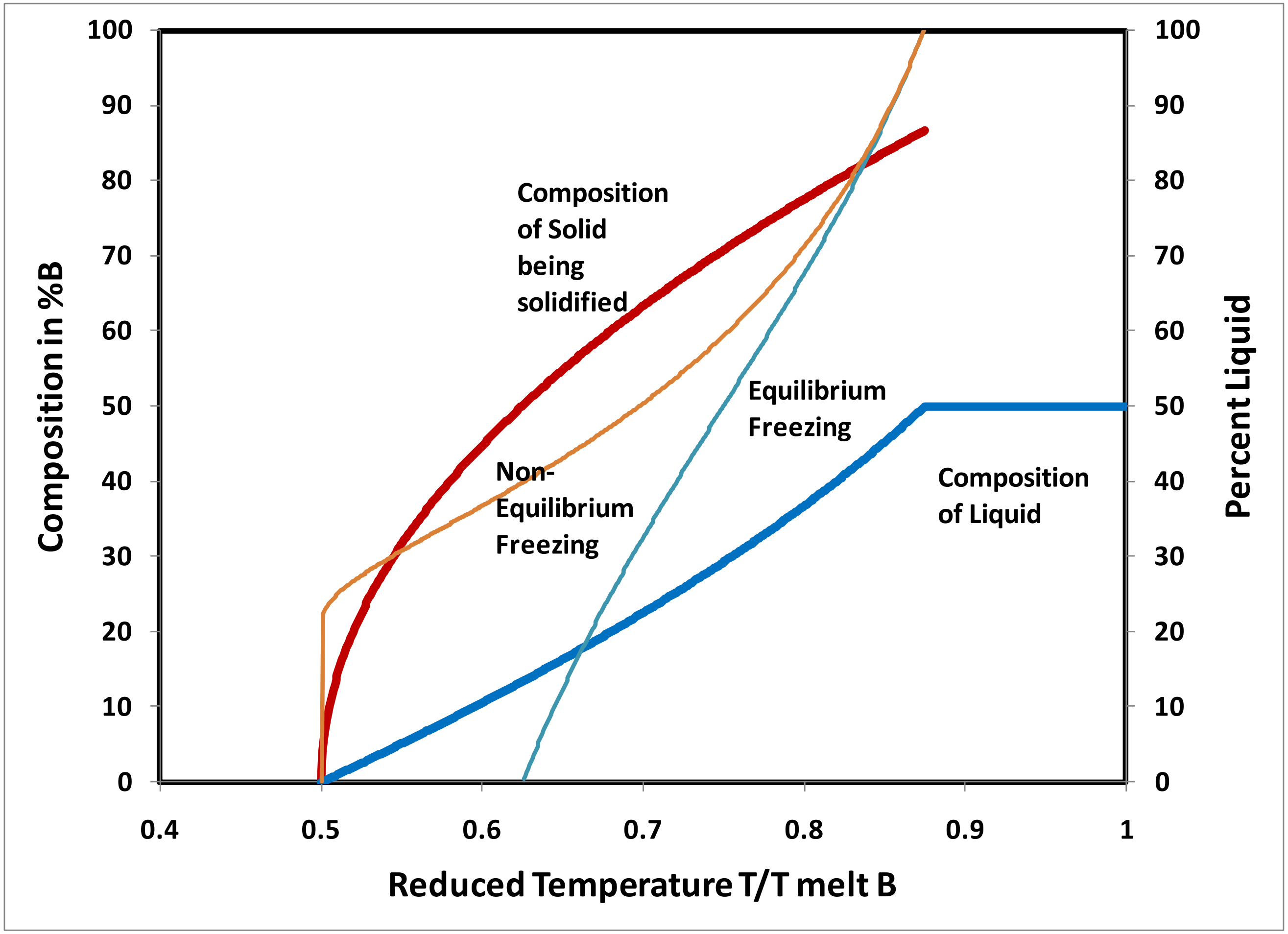


Solid solution

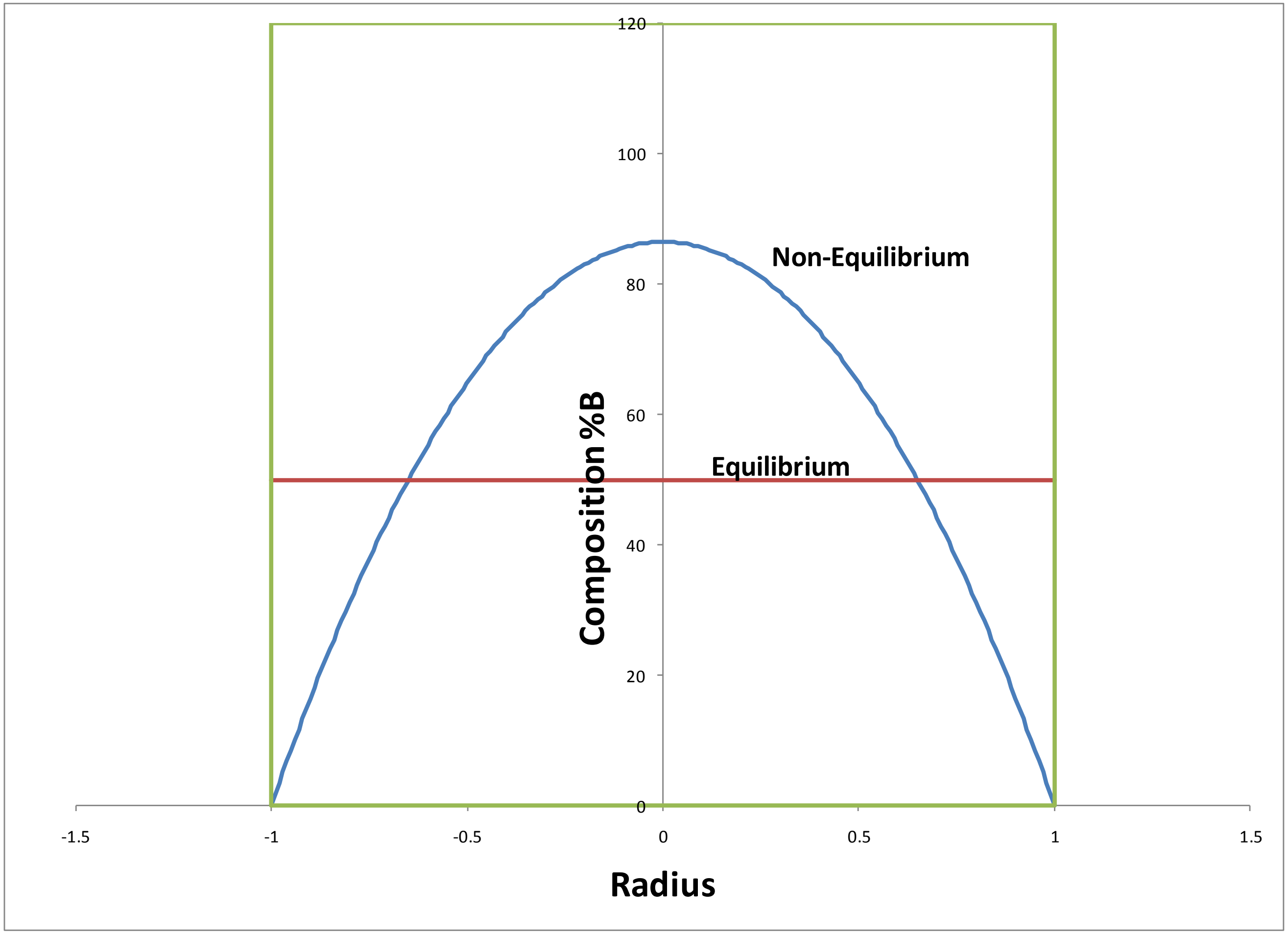




Non equilibrium freezing

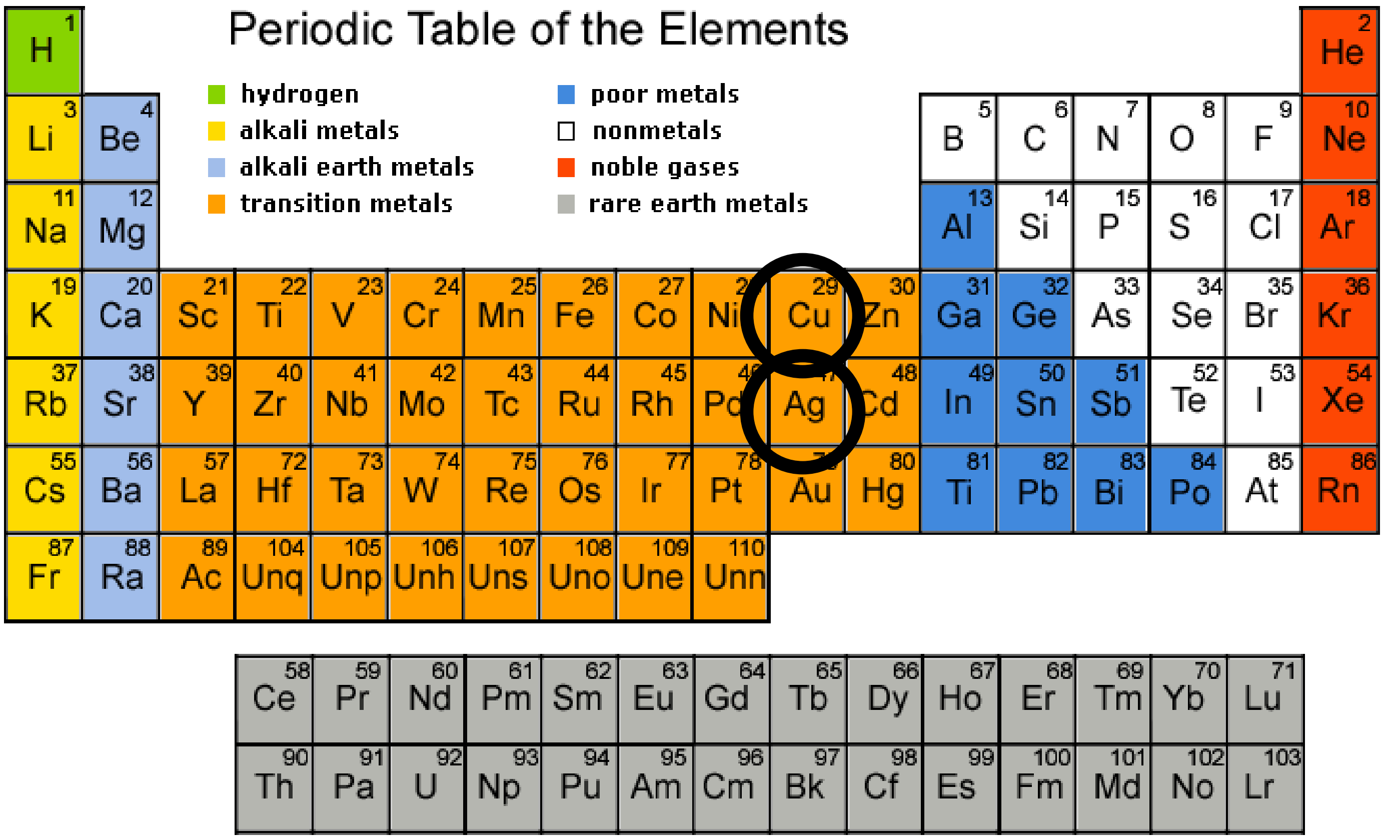


Coring

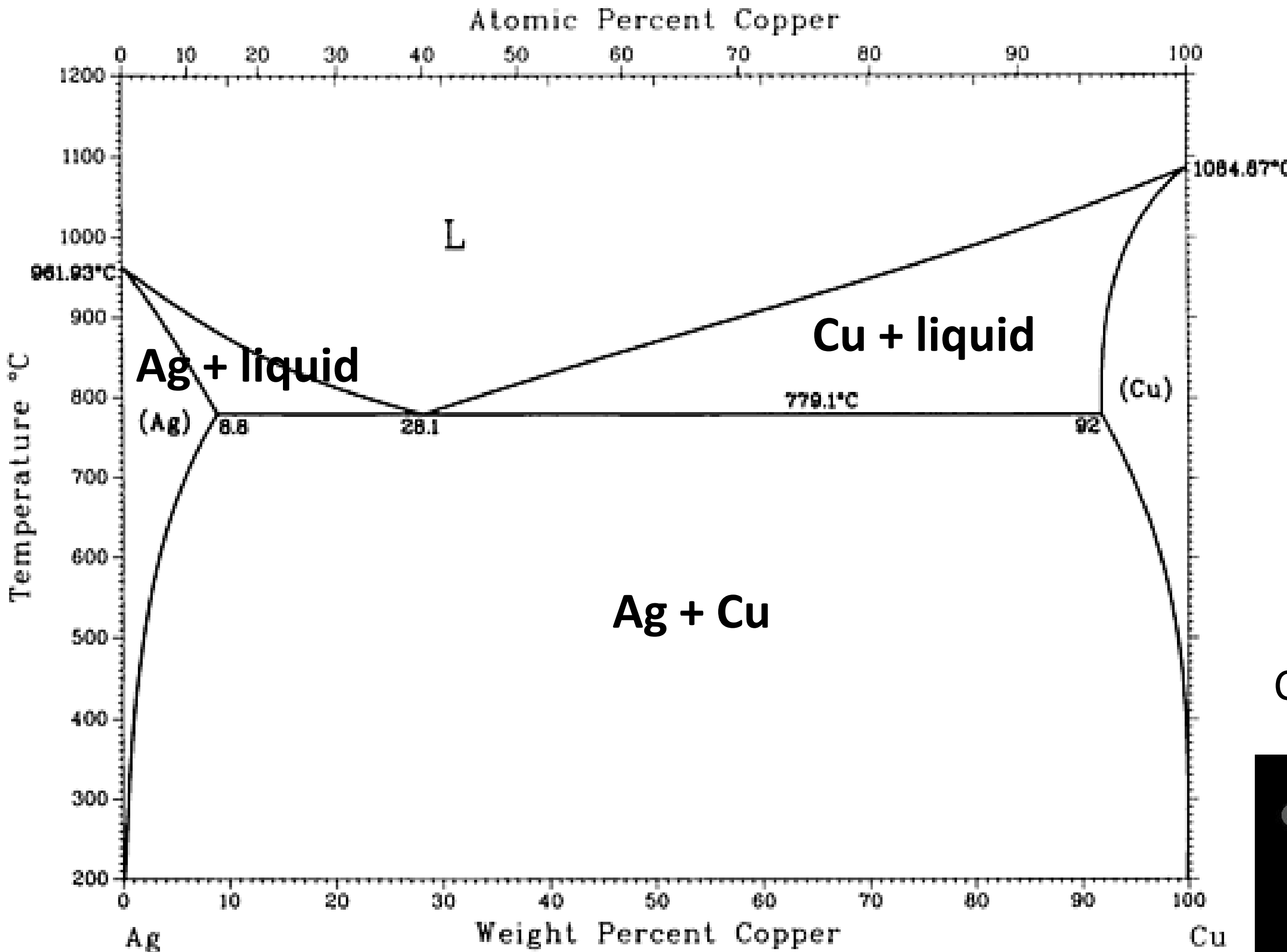


120
100
80
60
40
20
0
Non-Equilibrium
Equilibrium
Composition %B
-1.5
-1
-0.5
0
0.5
1
1.5
Radius

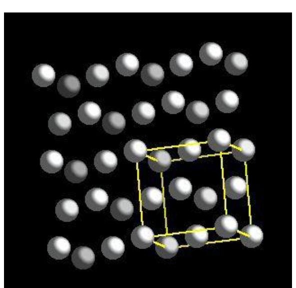
Two components



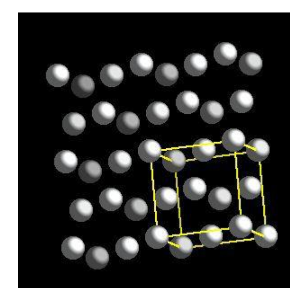
Eutectic



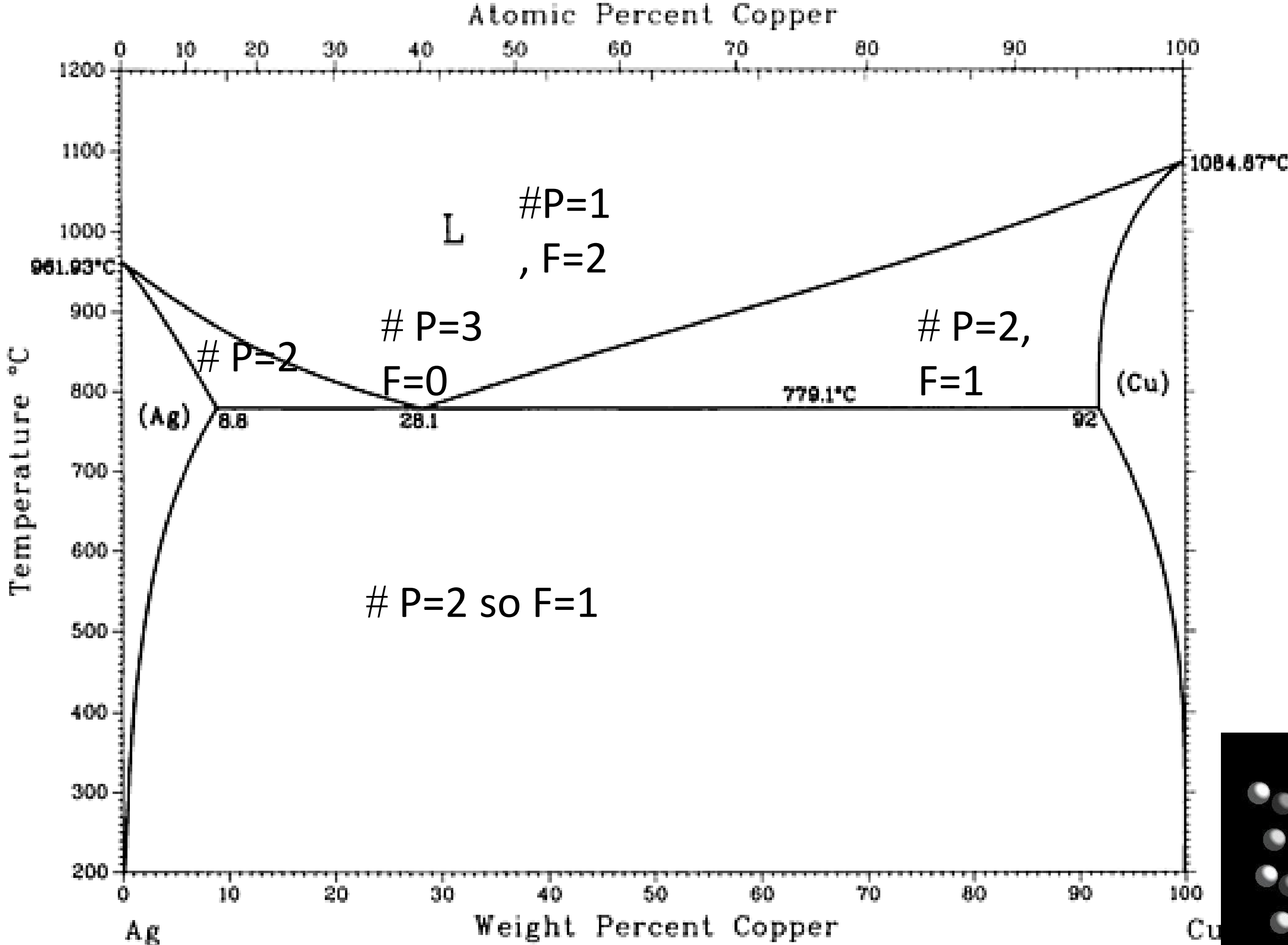
Ag^{+1} 1.26 Å



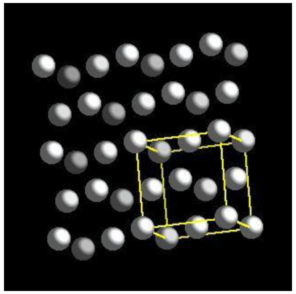
Cu^{+1} 0.96 Å

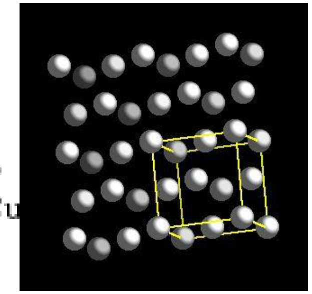


Binary C=2
n=1

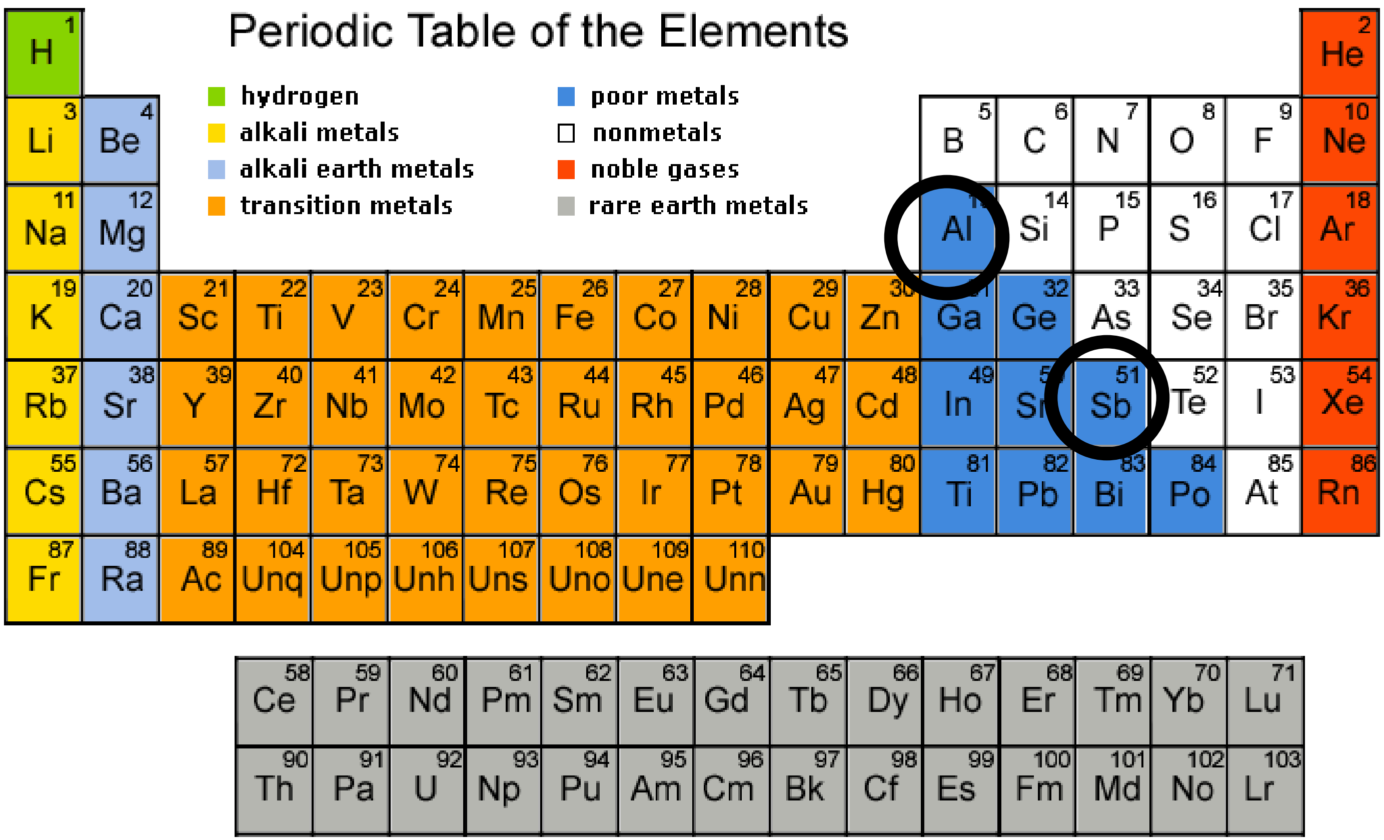


Atomic Percent Copper
0
10
20
30
40
50
60
70
80
90
100
1200
1100
1000
900
800
700
600
500
400
300
200
Temperature °C
1084.87°C
961.93°C
L
#P=1
, F=2
# P=3
F=0
# P=2
# P=2,
F=1
(Ag)
(Cu)
8.8
28.1
779.1°C
92
P=2 so F=1
0
10
20
30
40
50
60
70
80
90
100
Weight Percent Copper
Ag
Cu

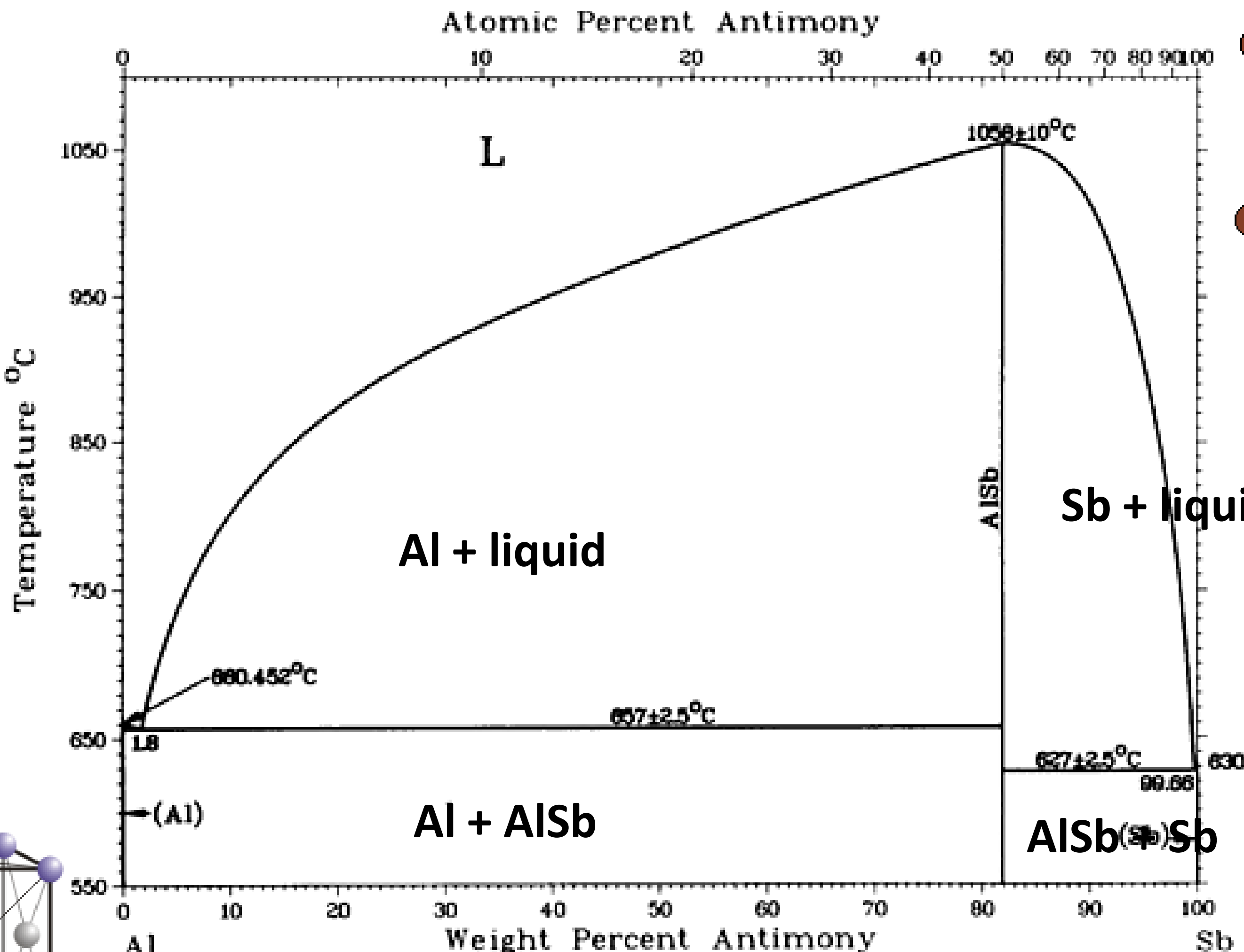


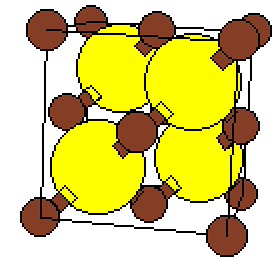


Two components

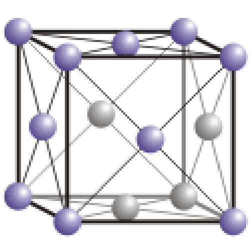


Congruently melting intermetalic compound

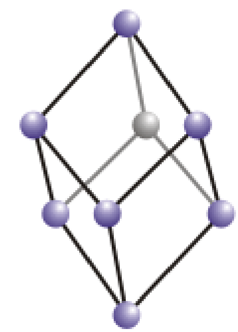




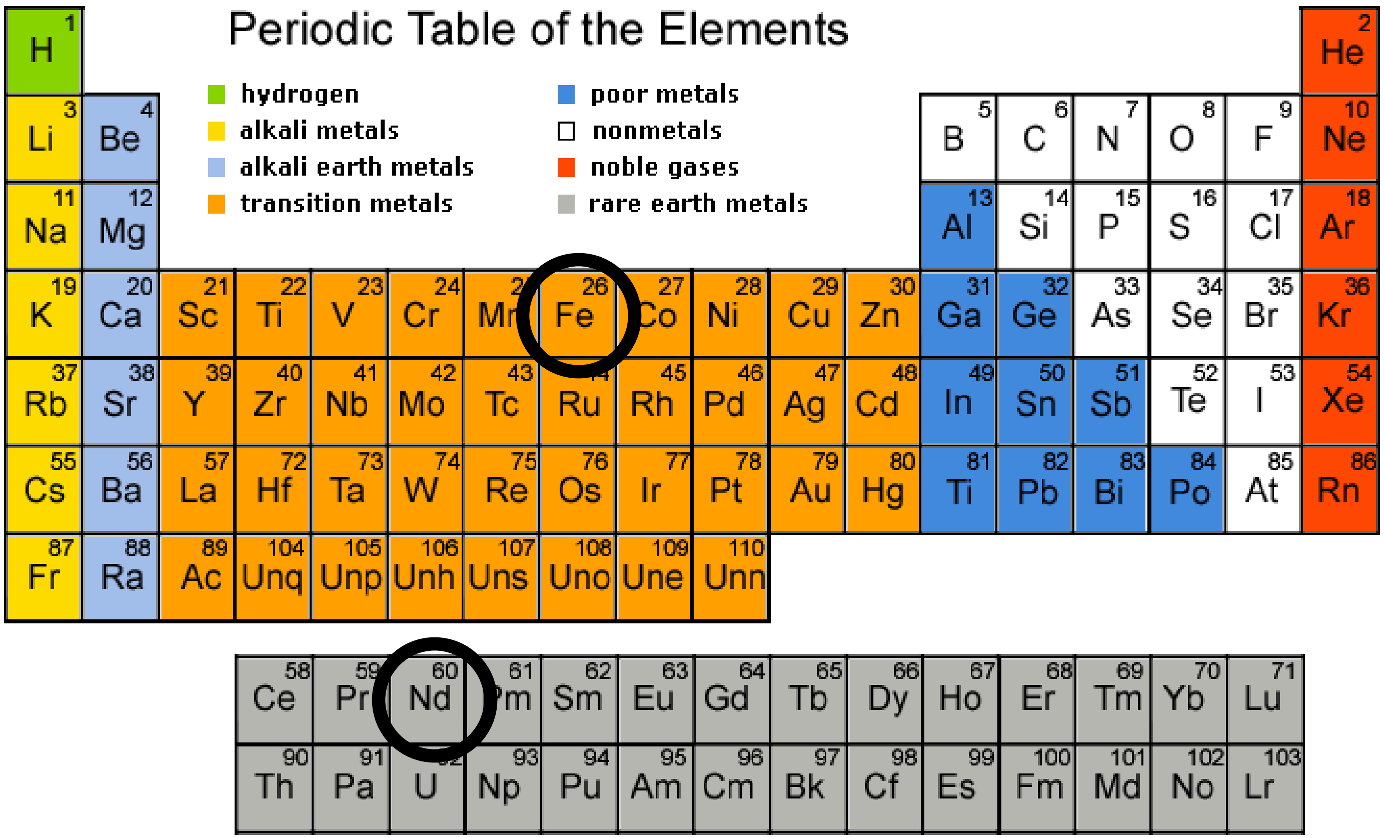
FCC



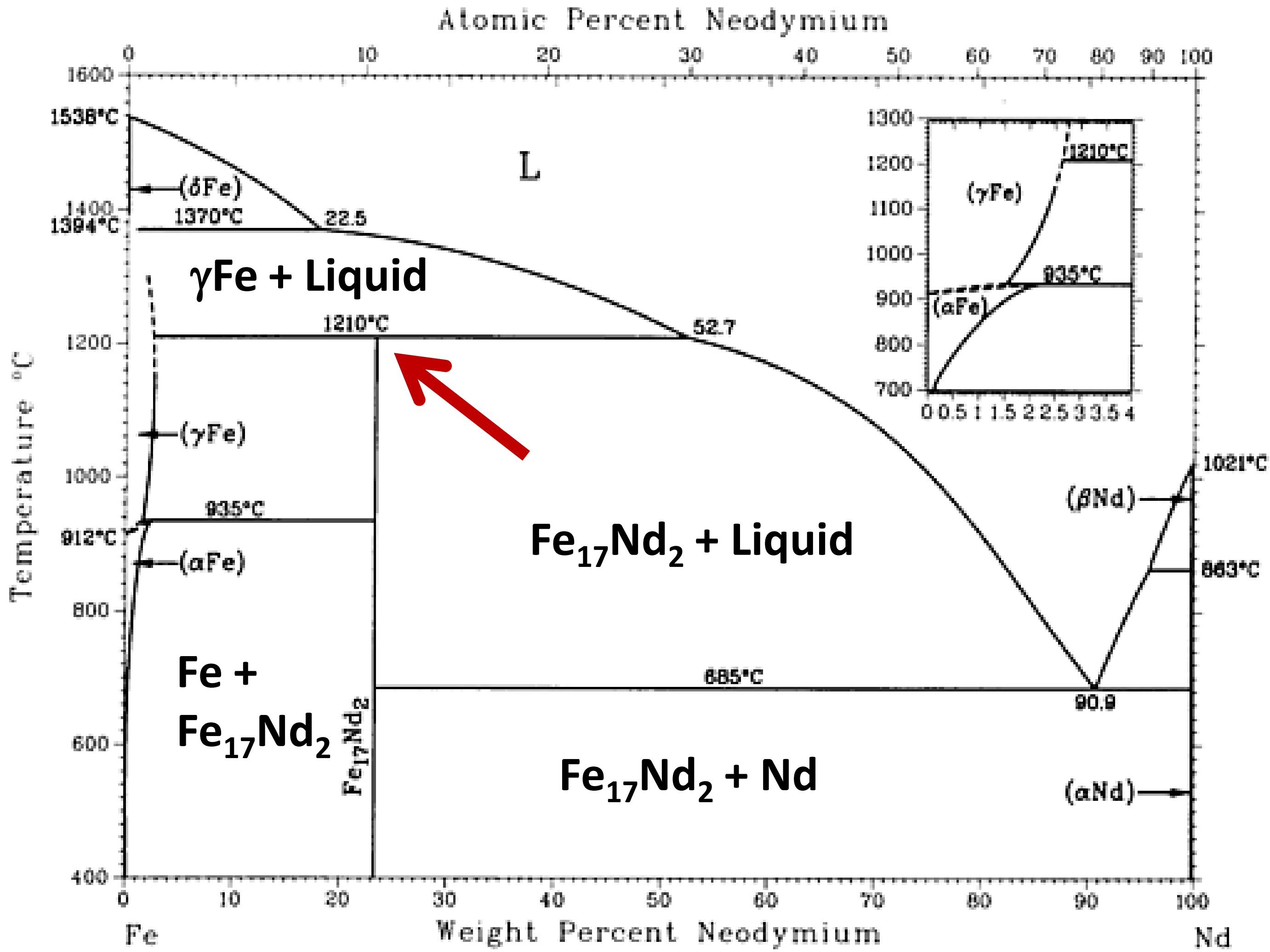
Rhombohedral



Two components

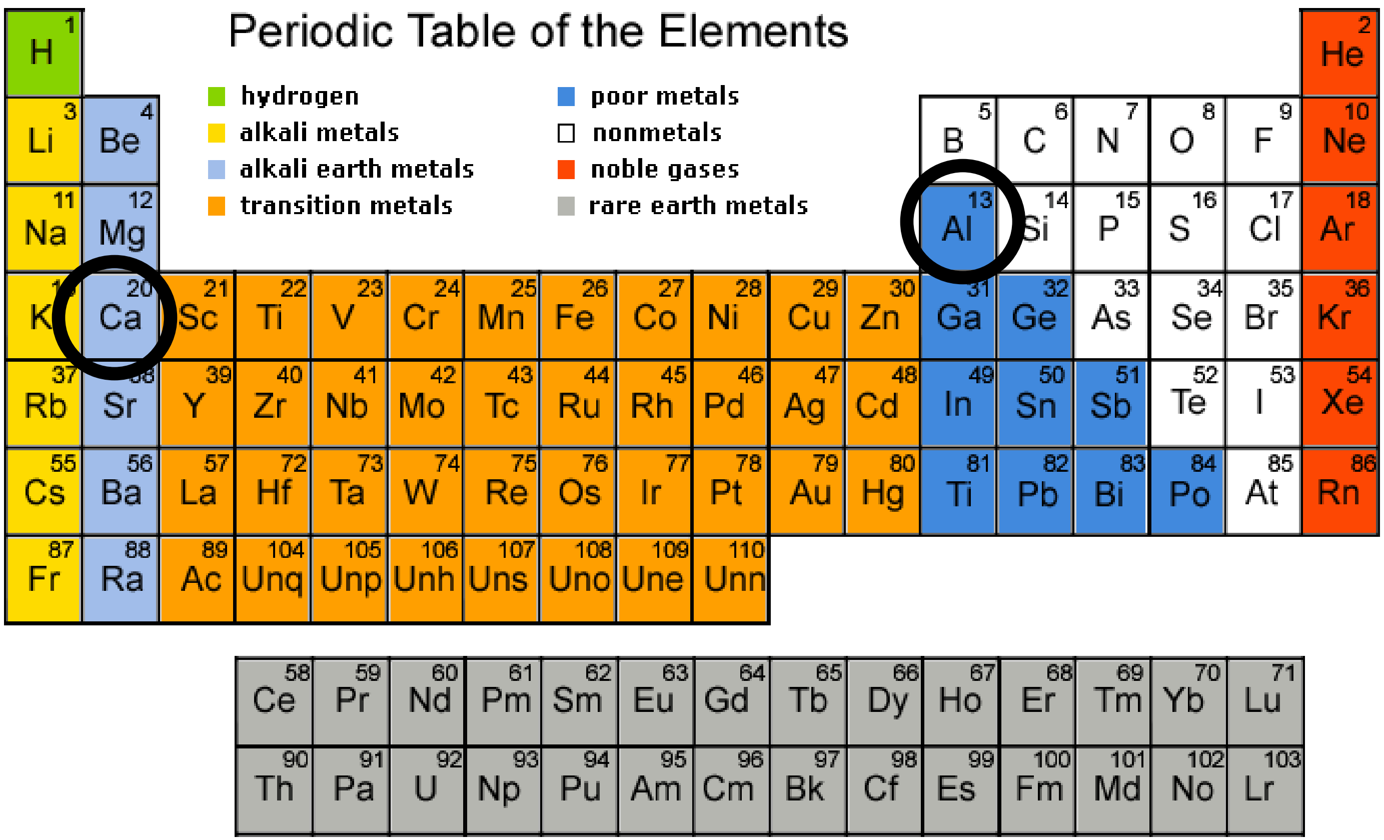


Peritectic



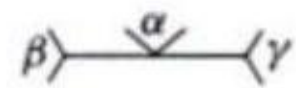
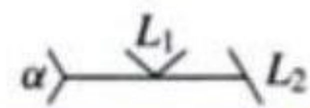
Atomic Percent Neodymium
Weight Percent Neodymium
Temperature °C
Fe
Nd
L
1538°C
(δFe)
1394°C
1370°C
22.5
γFe + Liquid
1210°C
52.7
(γFe)
935°C
912°C
(αFe)
Fe + Fe17Nd2
Fe17Nd2
Fe17Nd2 + Liquid
685°C
90.9
Fe17Nd2 + Nd
1021°C
(βNd)
863°C
(αNd)

Two components



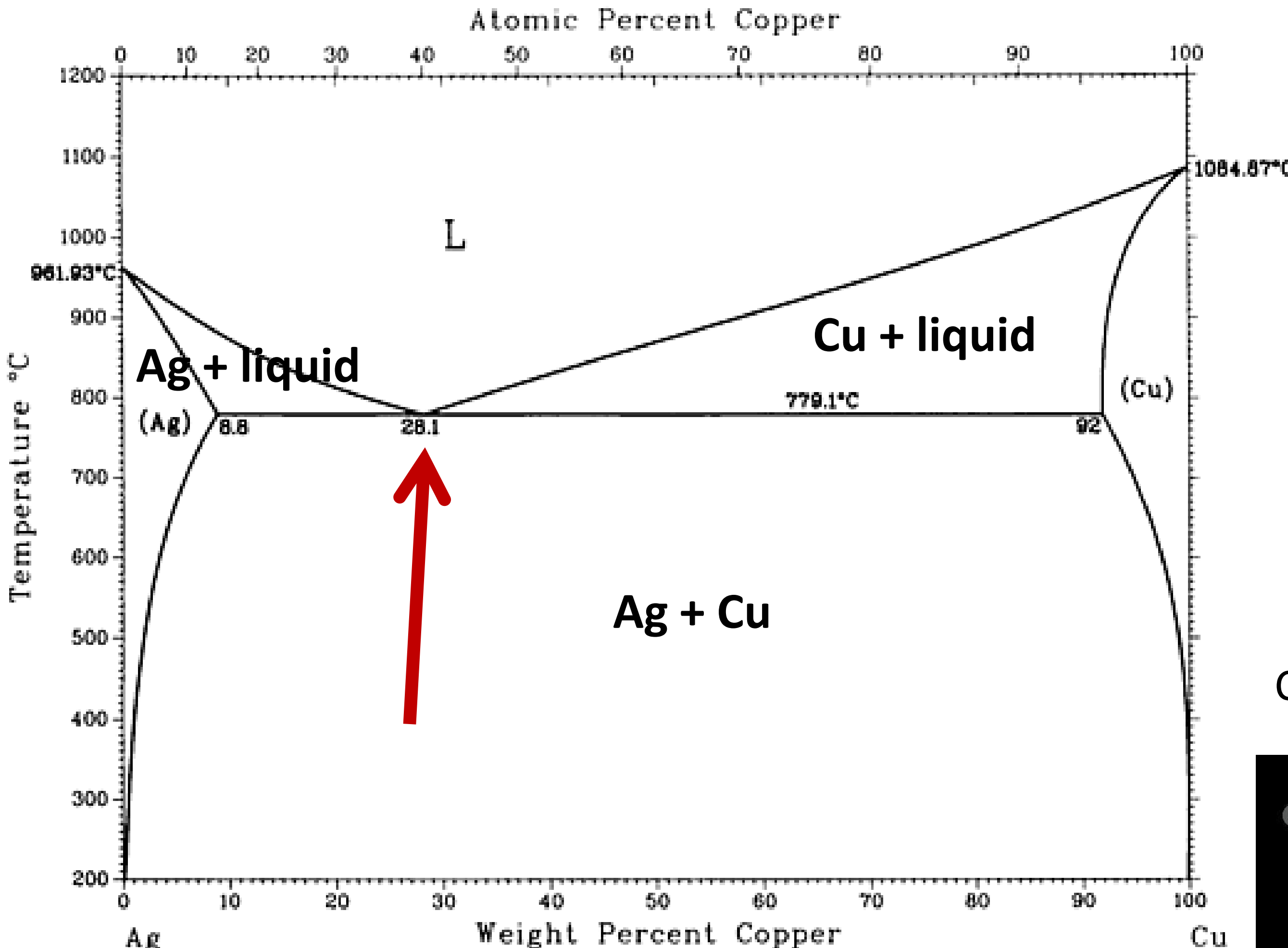
Invariant Reactions

Table 8.1 Types of Three-Phase Invariant Reactions Occurring in Binary Phase Diagrams

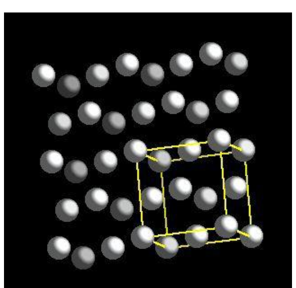
Name of reaction	Equation	Phase-diagram characteristic
Eutectic	$L \xrightarrow{\text{cooling}} \alpha + \beta$	
Eutectoid	$\alpha \xrightarrow{\text{cooling}} \beta + \gamma$	
Peritectic	$\alpha + L \xrightarrow{\text{cooling}} \beta$	
Peritectoid	$\alpha + \beta \xrightarrow{\text{cooling}} \gamma$	
Monotectic	$L_1 \xrightarrow{\text{cooling}} \alpha + L_2$	

Eutectic

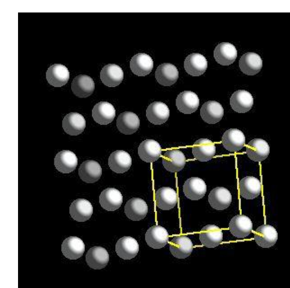
Liquid 1 ⇔ Solid 1 + Solid 2



Ag^{+1} 1.26 Å

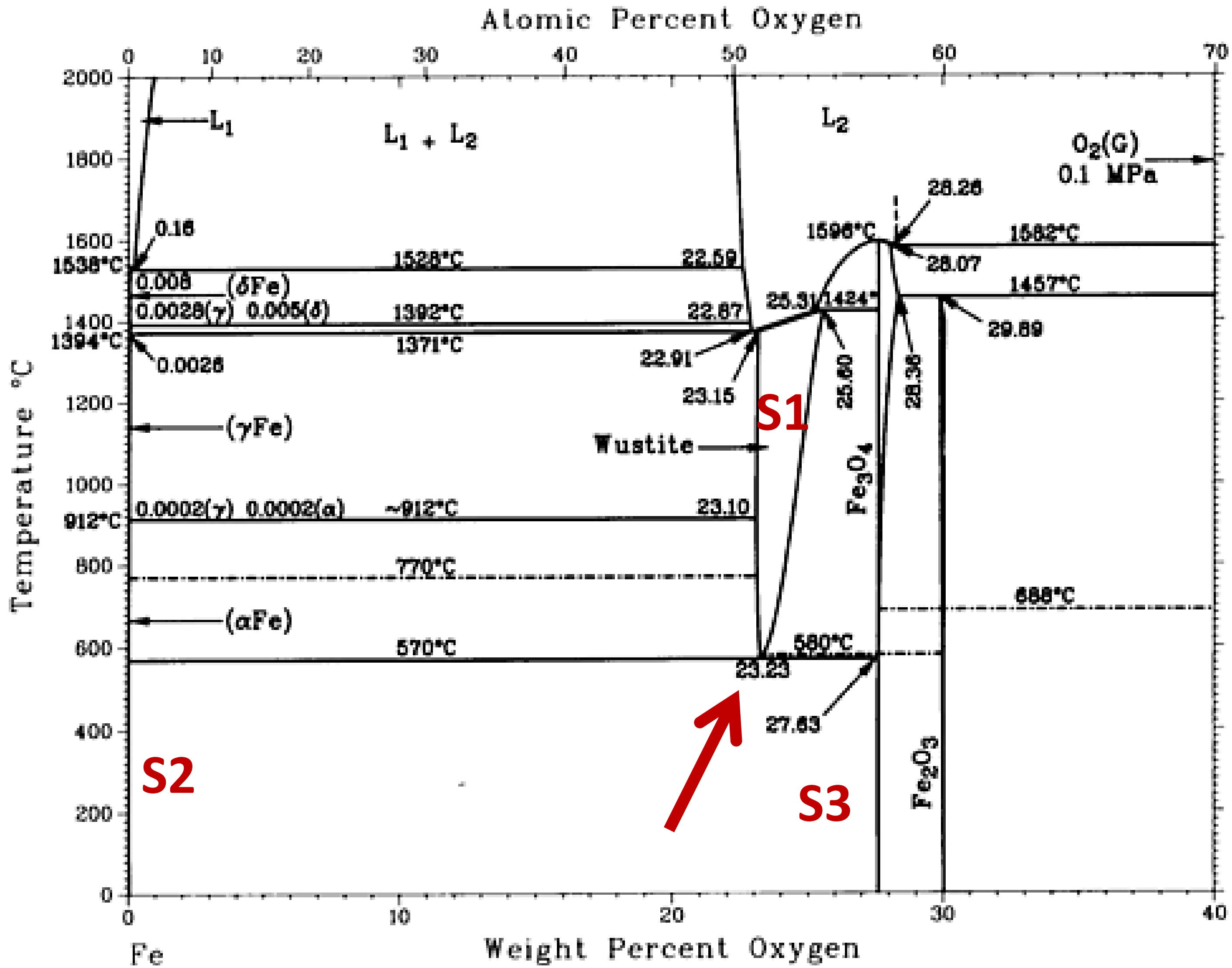


Cu^{+1} 0.96 Å

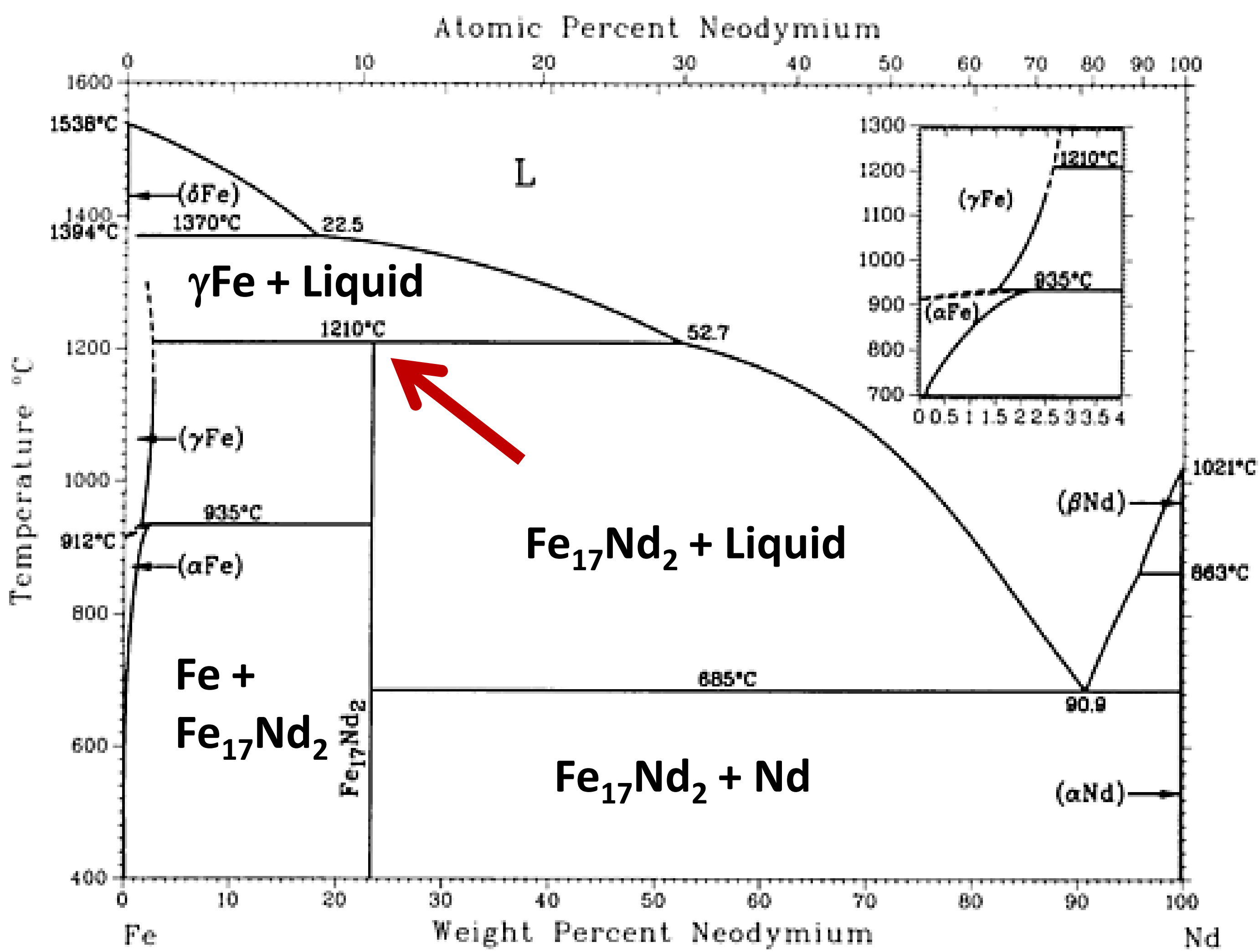


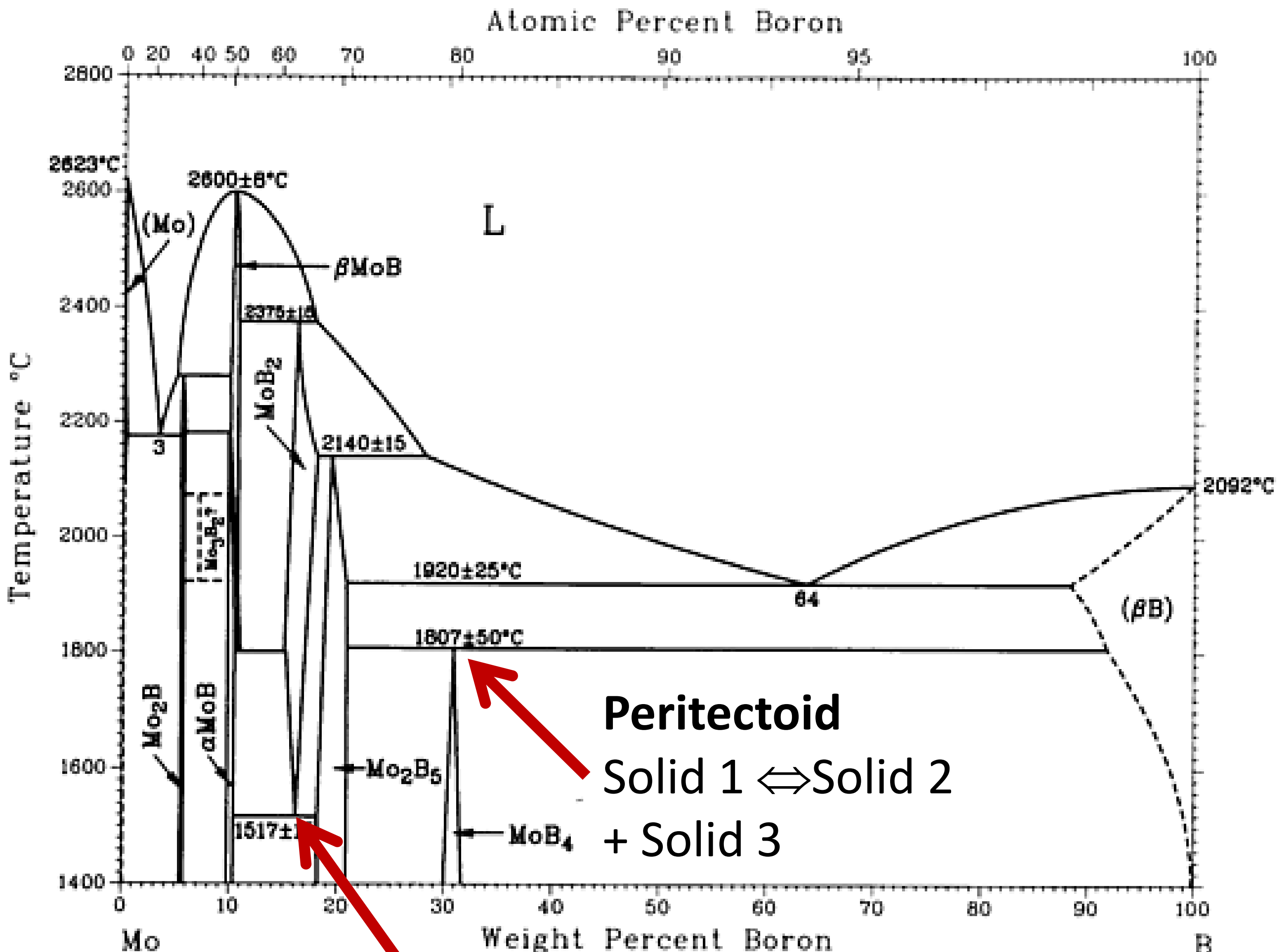
Eutectoid

solid 1 ⇔Solid 2 + Solid 3



Peritectic
Liquid⇔Solid + Liquid



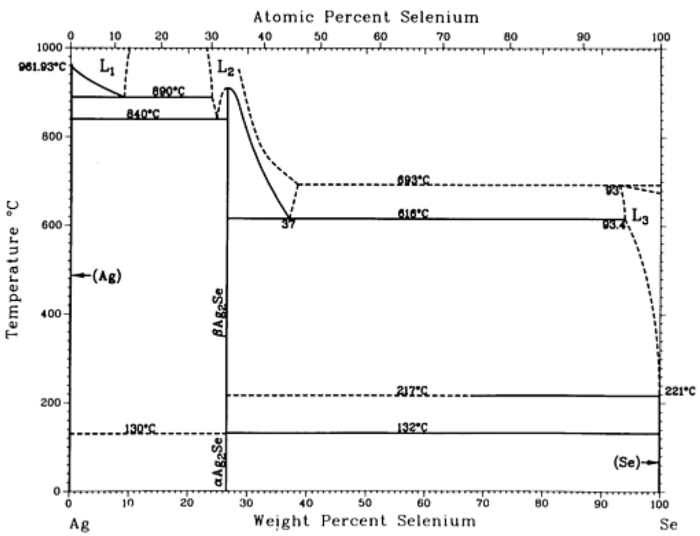


Peritectoid

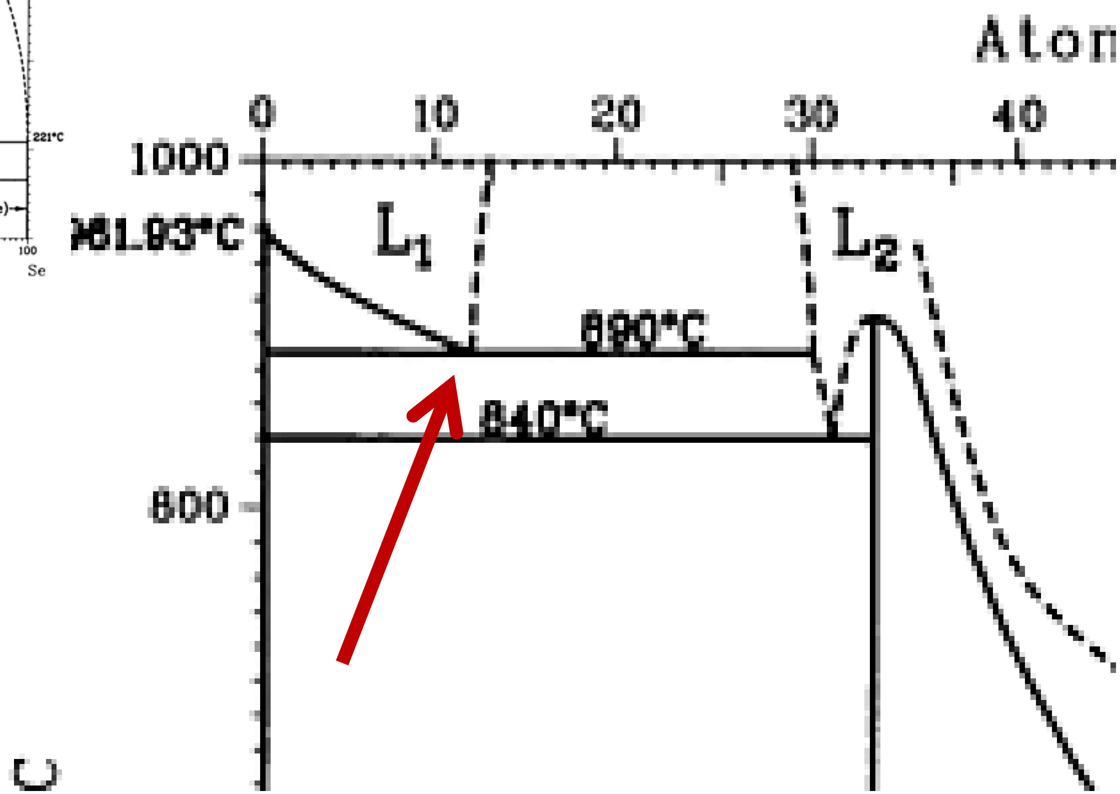
Solid 1 ⇔ Solid 2 + Solid 3

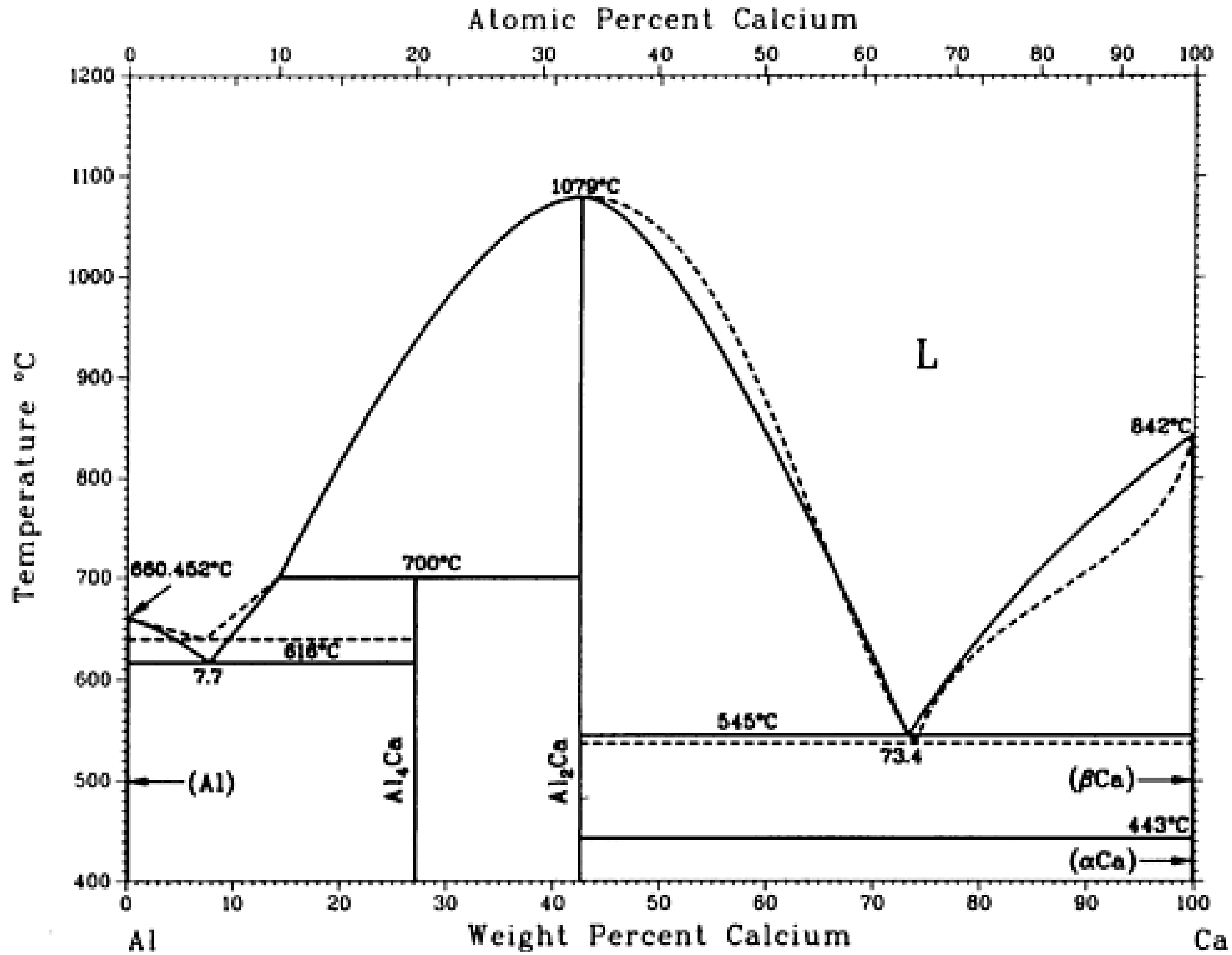
Eutectoid

Monotectic

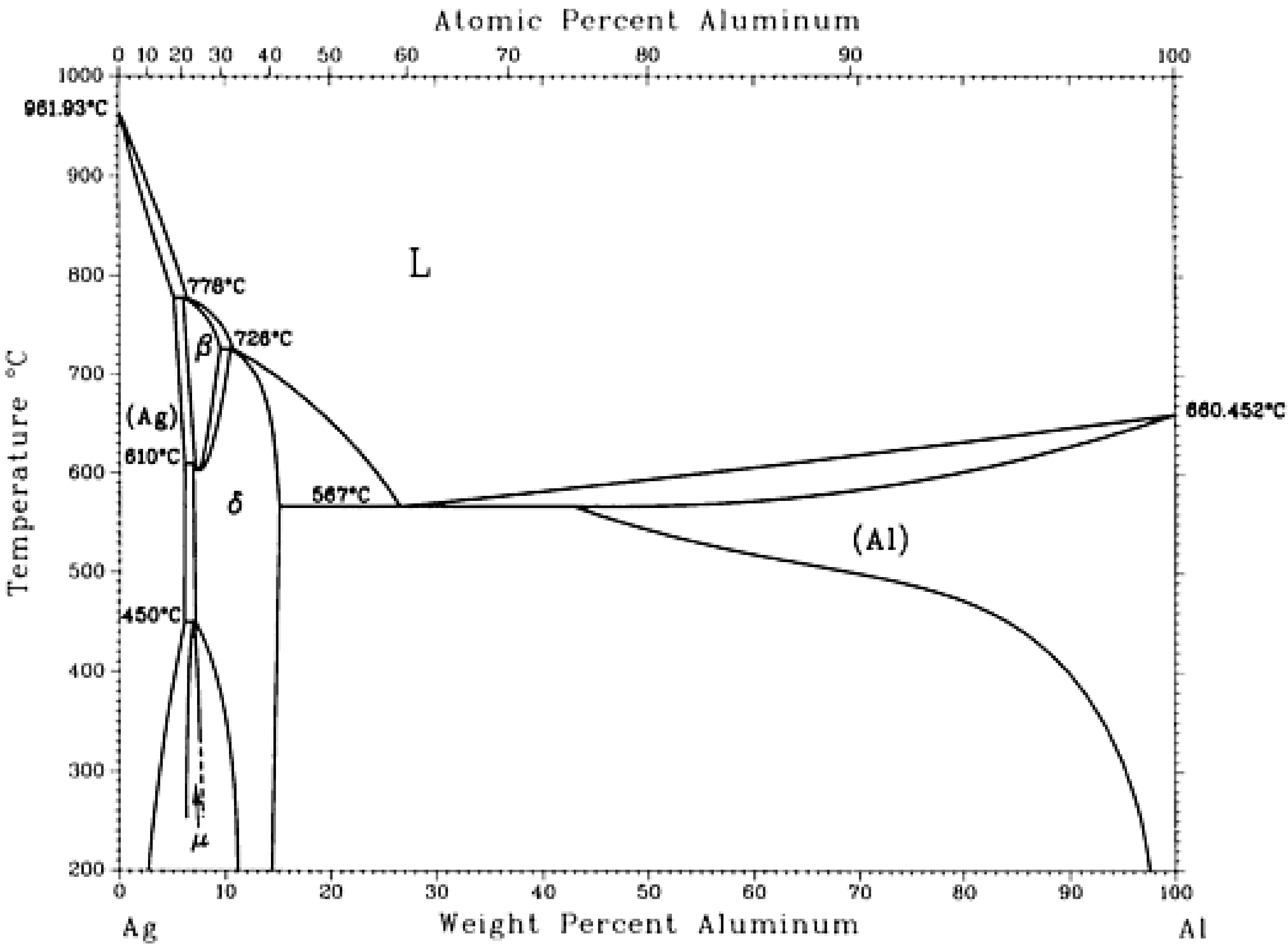


Liquid 1 ⇒ Solid + Liquid 2



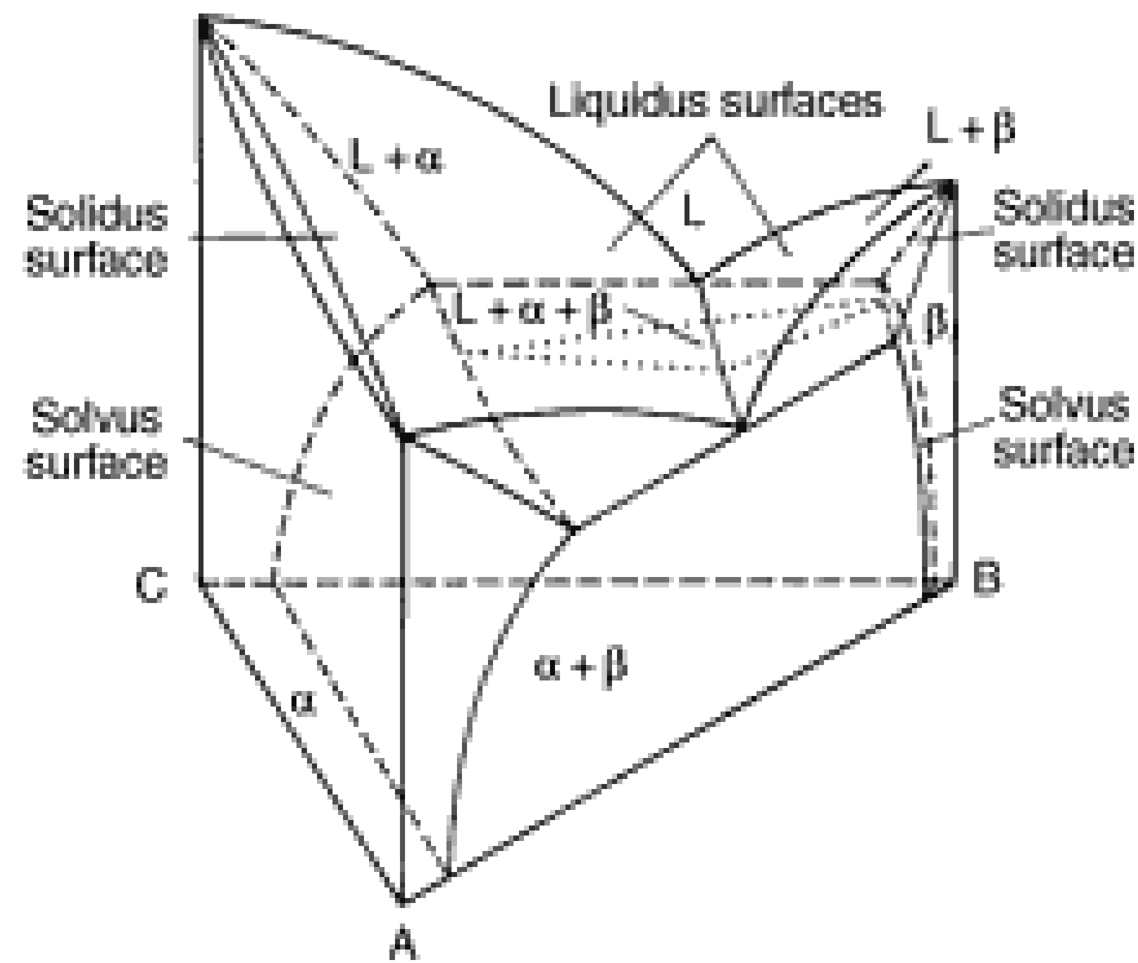


Dashed lines = calculated.

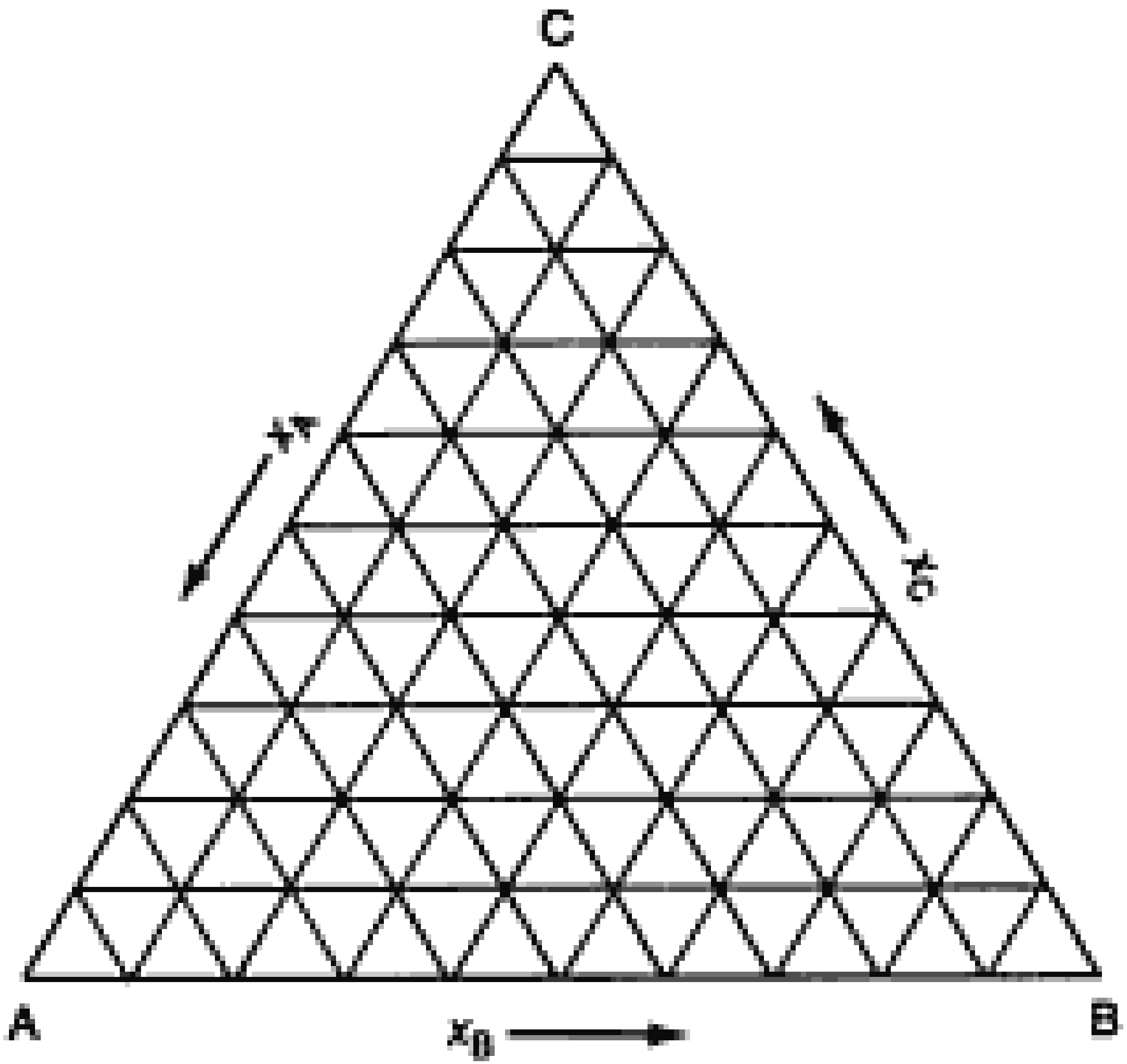


Atomic Percent Aluminum
0
10
20
30
40
50
60
70
80
90
100
1000
961.93°C
900
800
700
600
500
400
300
200
Temperature °C
L
778°C
726°C
β
(Ag)
610°C
δ
567°C
660.452°C
(Al)
450°C
μ
0
10
20
30
40
50
60
70
80
90
100
Weight Percent Aluminum
Ag
Al

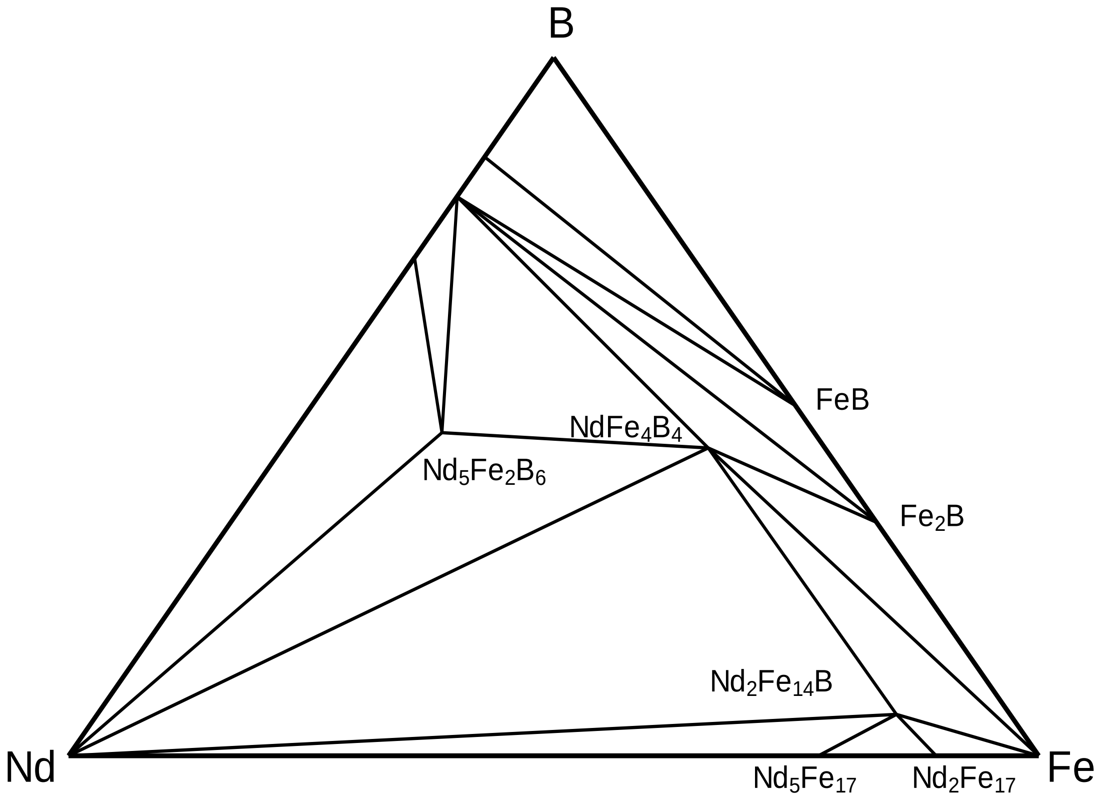
Ternary Phase Diagram

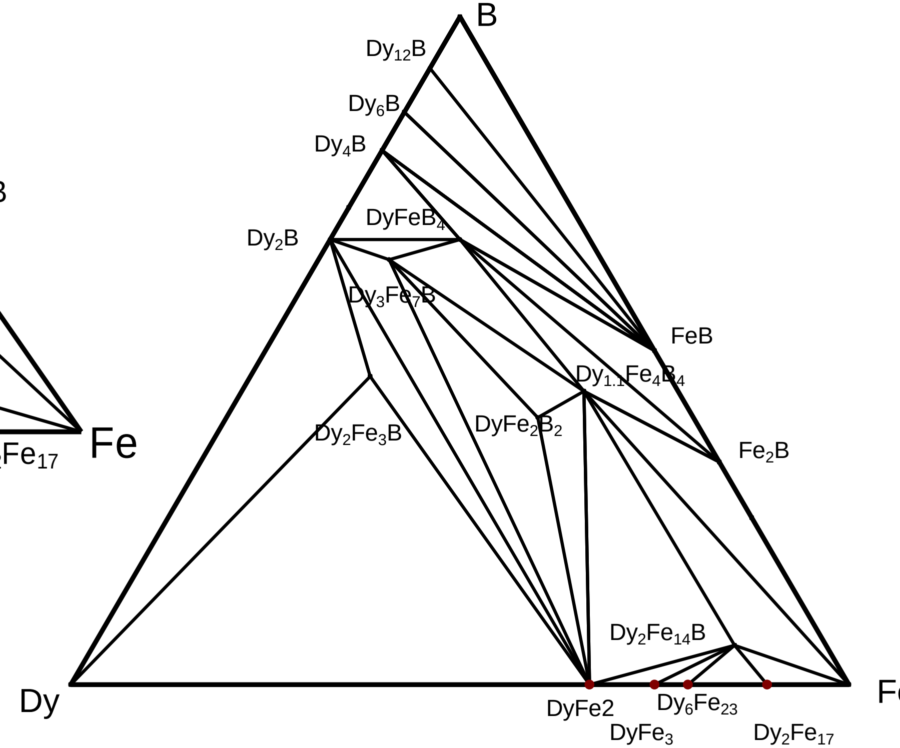


Ternary Isothermal Cut

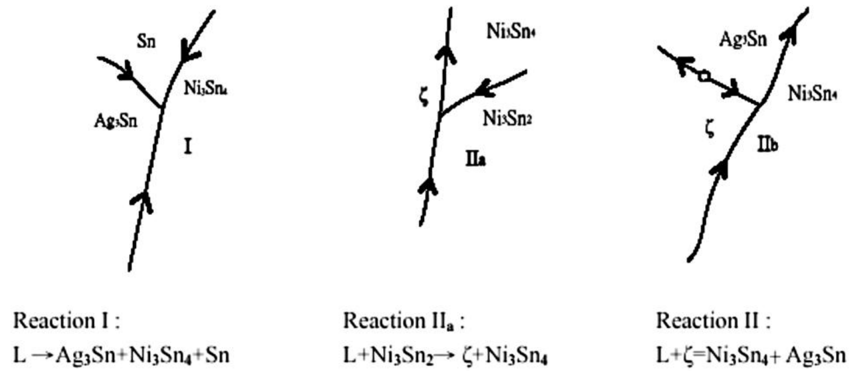


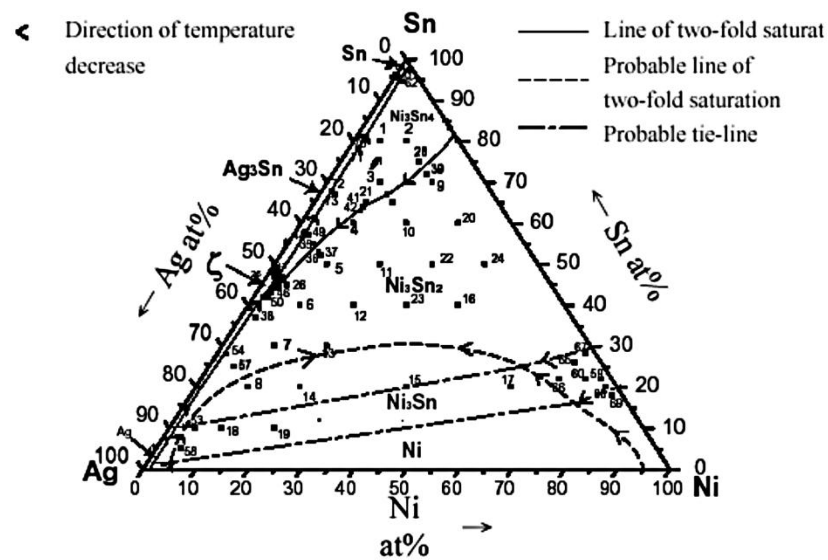
Typical ternary phase diagram at constant temperature





ternary liquidus projection





Liquidus projection of the Nb-Ti-Si system with isothermal lines